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METALLURGICAL CALCULATIONS

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METALLURGICAL CALCULATIONS

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ONE VOLUME EDITION

PART I

Introduction, Chemical and Thermal Principles
Problems in Combustion, and
Radiation and Conduction of Heat

PART II

Applications to the Metallurgy of Iron and Steel

PART III

Applications to Other Metals (Non-ferrous Metals)

THIRD IMPRESSION

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PREFACE

While issuing Parts I, II and III separately, for the use of students, it is thought that most persons, particularly practical metallurgists, will prefer to have the whole work in one volume.

The writer has endeavored to correct all the mistakes which crept into former editions, and to add such new and useful physical and chemical data as have appeared to date. Some new features are the tables of thermochemical constants (which will assist in predicting undetermined heats of formation), the estimation of many latent heats of fusion and vaporization of the elements (which data can be used *pro tem.* as first approximations), and the evaluation of vapor tension formulas for the elements in both liquid and solid states (likewise to be used as first approximations). My thanks are due to Mr. Leonard Buck and Mr. Y. Takikawa, students in metallurgy, for considerable assistance given in calculating and completing the new tabular data.

The author is grateful to many friends whose kindly criticisms have pointed out mistakes or suggested improvements. He appreciates the careful translations which have been made into Italian by Sr. Remo Catani, into Russian by Engineer Koshkin, into German by Prof. Neuman and Engineer Brodal, and regrets that the breaking out of the great war has interrupted translations already begun into French and Spanish. These international recognitions are simply proofs that the day of *Quantitative Metallurgy* is dawning all over the world, and that the application of *Metallurgical Calculations* is the path to *Metallurgical Efficiency.*

JOSEPH W. RICHARDS.

LEHIGH UNIVERSITY,
January 15, 1918.

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CONTENTS.

	Page
Introduction.—Scope of the Treatise	iii–xi
Chapter I.—The Chemical Equation	1–12
Atomic Weights	1
Relative Weights	2
Relative Volumes of Gases	2
Exact Weights and Exact Volumes	3
Weights and Volumes of Gases	4
Corrections for Temperature	5
Corrections for Pressure	7
Corrections for Temperature and Pressure	7
Problem 1.—Combustion of Coal	8
Problem 2.—Combustion of Natural Gas	10
Problem 3.—Oxidation in a Bessemer Converter	11
Chapter II.—The Applications of Thermochemistry	13–40
Thermochemical Nomenclature	13
Thermochemical Data	18–40
Oxides	18
Hydrates	19
Sulfides	21
Selenides, Tellurides	22
Arsenides, Antimonides, Phosphides, Nitrides	23
Hydrides, Hydrocarbons	24
Carbides	25
Silicides, Fluorides	26
Chlorides	27
Carbonates	28
Bi-Carbonates	29
Nitrates	30
Silicates	31
Sulphates	32
Bi-sulphates, Phosphates, Arsenates, Tungstates	33
Borates, Molybdates, Titanates	34
Manganates, Aluminates, Cyanides	35
Cyanates, Metallo-cyanides	36

Amalgams, Alloys..... 37
Thermochemical Constants of Bases and Acids. 38

CHAPTER III.—THE USE OF THE THERMOCHEMICAL DATA. 41–60
Simple Combinations—Complex Combinations..... 41
Double Decompositions..... 43
Calorific Power of Fuels..... 46
Problem 4.—Combustion of Natural Gas..... 47
Dulong's Formula..... 48
The Theoretical Temperature of Combustion..... 50
Specific Heats of Gases Produced..... 51
Combustion with Heated Fuel or Air..... 52
Problem 5.—Calorific Intensity of Natural Gas. 54
The Eldred Process of Combustion..... 55
Temperatures in the "Thermit Process"..... 58

CHAPTER IV.—THE THERMOCHEMISTRY OF HIGH TEMPERATURES 61–117
Reduction of Zinc Oxide by Carbon..... 63
General Remarks..... 68
Reduction of Iron Oxide by Hydrogen..... 69
Specific Heats of the Elements..... 70
Latent Heats of Fusion of the Elements..... 71
Latent Heats of Vaporization of the Elements..... 73
Thermophysics of the Elements..... 74
Tables of Thermophysics of the Elements.....75–103
Efficiency of Furnaces..... 104
Problem 6.—Efficiency of a Rockwell Furnace.. 106
Problem 7.—Efficiency of an Amalgam Retort.. 107
Problem 8.—Efficiency of a Zinc Distilling Furnace..... 108
Thermophysics of Alloys..... 109
Tables of Thermophysics of Alloys.....109–113
Problem 9.—Efficiency of a Steel Melting Furnace..... 114
Problem 10.—Efficiency of a Siemen's Furnace.. 114
Problem 11.—Efficiency of a Foundry Air-furnace..... 114
Problem 12.—Efficiency of a Foundry Cupola.. 115

CHAPTER V.—THERMOPHYSICS OF CHEMICAL COMPOUNDS 118–144
Oxides..... 118

Problem 13.—Efficiency of Alumina Melting Furnace..... 127
Problem 14.—Reduction of Iron Oxides by CO gas..... 128
Problem 15.—Reduction of Iron Oxides by Carbon..... 129
Chlorides..... 131
Bromides, Iodides..... 133
Fluorides, Sulfides..... 134
Compound Sulfides..... 135
Arsenides, Antimonides, Selenides, Tellurides..... 136
Cyanides, Hyposulfites, Sulfates..... 136
Carbonates, Nitrates..... 137
Borates, Phosphates, Chromates, Arsenates..... 138
Chlorates, Aluminates, Titanates, etc..... 139
Silicates..... 139
Miscellaneous Materials..... 142
Slags..... 144

CHAPTER VI.—ARTIFICIAL FURNACE GAS.....145–184
Simple Producers..... 146
Problem 16.—Investigation of a Simple Producer..... 149
Problem 17.—Drying of Moist Producer Gas... 154
Mixed Gas Producers..... 158
Problem 18.—Investigation of a Morgan Producer..... 163
Mond Gas..... 169
Problem 19.—Calculations on a Mond Producer. 169
Reactions on Pre-heating Mond Gas..... 175
Water Gas..... 177
Problem 20.—On a Dellwick-Fleischer Plant.... 179
Problem 21.—Blast Required for D-F. Plant... 182

CHAPTER VII.—CHIMNEY DRAFT AND FORCED DRAFT.. 185–199
Chimney Draft..... 185
Available Head..... 191
Problem 22.—Design of Puddling Furnace Chimney..... 192
Problem 23.—Raising Steam by Waste Heat... 194

CHAPTER VIII.—CONDUCTION AND RADIATION OF HEAT. 186–200
Principles of Heat Conduction..... 200
Table of Heat Conductivities of Metals..... 203
Principles of Heat Transfer..... 206
Problem 24.—Cooling of Hot Air in a Tube 208
Table of Heat Conductivities of Insulating Materials..... 211
Radiation..... 213
Table of Radiating Capacity (Emissivity)..... 215

APPENDIX.....217–231
Problem 25.—Combustion of Hydrocarbons..... 217
Problem 26.—Calorific Values of Coal, Oil and Gas.. 219
Problem 27.—Calorific Values of Various Gases..... 219
Problem 28.—Combustion of Coal under a Boiler... 220
Problem 29.—Combustion of Anthracite Coal..... 221
Problem 30.—Air Required for Powdered Coal..... 221
Problem 31.—Efficiency Test on a Boiler..... 222
Problem 32.—Temperature of Powdered-coal Flame. 223
Problem 33.—Temperature at Tuyeres in Blast Furnace..... 223
Problem 34.—Efficiency of Powdered Coal Firing... 224
Problem 35.—Calculation of Chimney Draft..... 224
Problem 36.—Calorimeter Test of Temperature..... 224
Problem 37.—Calorimeter Test for Specific Heat.... 225
Problem 38.—Economy of a Feed-water Heater..... 225
Problem 39.—Working of Gas-engine..... 226
Problem 40.—Efficiency of a Gas Producer..... 226
Problem 41.—Temperature of Producer-gas Flame.. 227
Problem 42.—Drying Kiln for Peat..... 227
Problem 43.—Power from Waste Coke-oven Gases.. 228
Problem 44.—Efficiency of By-product Coke Ovens. 229
Problem 45.—Decomposition of Steam in a Producer. 229
Problem 46.—Chimney for a Gas Furnace..... 230
Problem 47.—Loss of Heat through Sides of Chimney 231

CONTENTS TO PART II.

PAGE

CHAPTER I.—BALANCE SHEET OF THE BLAST FURNACE . . 235–249
- Fuel 236
- Ore 239
- Flux 243
- Blast 244
  - Problem 51.—Balance of a Swedish Furnace . . . 245

CHAPTER II.—CALCULATION OF A FURNACE CHARGE . . 250–267
- Flux and Slag 251
  - Problem 52.—Calculation of Flux needed 259
- Comparison of Values of Fuels 261
- Comparison of Values of Fluxes 263
- Comparison of Values of Ores 265
  - Problem 53.—Cost of Pig Iron calculated 267

CHAPTER III.—UTILIZATION OF FUEL IN THE BLAST FURNACE 268–280
  - Problem 54.—Generation of Heat in Blast Furnace 268
  - Problem 55.—Efficiency of Hot Blast Stoves 270
  - Problem 56.—Power from Blast Furnace Gases . 272
- Grüners Ideal Working 274
- Minimum Carbon necessary in the Furnace 277

CHAPTER IV.—HEAT BALANCE SHEET OF BLAST FURNACE 281–304
- Heat received and developed 281
  - Combustion of Carbon.—Illustration 281
  - Sensible Heat in Hot Blast.—Illustration 284
  - Formation of Pig Iron 285
  - Formation of Slag 286

PAGE

Heat absorbed and disbursed..... 287
Heat in Waste Gases..... 287
Heat in Slag..... 288
Heat in Pig Iron..... 289
Heat conducted away and radiated..... 289
Heat in Cooling Water..... 290
Heat for drying and dehydrating charges..... 290
Heat for decomposing carbonates..... 291
Heat for reduction of iron oxides..... 292
Heat for reduction of other oxides..... 292
Decomposition of Moisture of Blast..... 293
Problem 57.—Complete Heat Balance Sheet.... 294

CHAPTER V.—RATIONALE OF HOT-BLAST AND DRY-BLAST 305–312
Problem 58.—(for practice) Heat Balance Sheet. 305
Hot Blast.—Temperatures obtained..... 308
Dried Blast.—Increased Temperatures obtained..... 309
Illustration: Temperatures in a specific case.... 310
Table of temperatures under various conditions. 312

CHAPTER VI.—PRODUCTION, HEATING AND DRYING OF BLAST.....313–332
Production of blast. Work required..... 313
Problem 59.—Work of a blowing engine..... 315
Measurement of pressure of blast. Indicator cards.. 317
Heating of the blast..... 318
Problem 60.—Efficiency of an iron-pipe stove... 320
Problem 61.—Efficiency of fire-brick stoves..... 322
Drying air blast..... 325
Illustration: Increased efficiency of blowing engines..... 326
Illustration: Refrigeration required..... 326
Problem 62.—Efficiency of drying apparatus... 327
Illustrations: Calculation of saturation temperature..... 331
Problem 63.—Cooling compressed air by river water..... 331

CHAPTER VII.—THE BESSEMER PROCESS.....333–350
Air required..... 333
Problem 64.—Maximum and minimum blast... 334

PAGE

Air received..... 336
Problem 65.—Volume efficiency of blowing plant 336
Blast pressure..... 340
Illustration: Back pressure in converter..... 341
Problem 66.—Distribution of blast pressure.... 343
Flux and Slag..... 346
Illustration: Lime needed in a basic blow..... 347
Recarburization..... 348
Problem 67.—Recarburization balance sheet.... 349

CHAPTER VIII.—THERMO-CHEMISTRY OF THE BESSEMER PROCESS.....351–367
Elements consumed..... 351
Heat balance sheet—items..... 353
Heat developed by oxidation..... 356
Heat of formation of slag..... 357
Illustration: Heat of formation of basic slag.... 358
Heat in escaping gases..... 360
Heat conducted to the air..... 362
Heat radiated..... 363
Problem 68.—Complete heat balance sheet..... 363

CHAPTER IX.—THE TEMPERATURE INCREMENT IN THE BESSEMER CONVERTER.....368–380
Combustion of Silicon..... 369
Combustion of Manganese..... 371
Combustion of Iron..... 372
Combustion of Titanium..... 373
Combustion of Aluminum, Nickel, Chromium..... 374
Combustion of Carbon..... 375
Combustion of Phosphorus..... 377
Résumé..... 379

CHAPTER X.—THE OPEN-HEARTH FURNACE.....381–395
Gas producers..... 381
Flues to furnace; regenerators..... 382
Problem 69.—Sizes of regenerators..... 384
Valves and ports..... 388
Problem 70.—Areas of gas and air ports..... 389
Laboratory of furnace..... 391

PAGE

Problem 71.—Efficiency of laboratory..... 393
Chimney flues and chimney, miscellaneous..... 395

CHAPTER XI.—THERMAL EFFICIENCY OF OPEN-HEARTH FURNACES.....396–428
Heat in warm charges; in gas used..... 397
Heat in air used..... 398
Heat of combustion; of oxidation of the bath..... 399
Heat of formation of slag; heat in melted steel..... 399
Reduction of iron ore; decomposition of carbonates.. 400
Heat in slag..... 401
Loss by imperfect combustion; in chimney gases.... 402
Loss by conduction and radiation..... 403
Problem 72.—Heat balance sheet..... 403
Problem 73.—Thermal efficiencies..... 411
Problem 74.—New Siemens' furnace..... 418
Problem 75.—The Monell process..... 424

CHAPTER XII.—THE ELECTROMETALLURGY OF IRON AND STEEL.....429–451
Electrothermal reduction of iron ores..... 429
Problem 76.—Production of pig-iron electrically. 430
Problem 77.—Production of nickeliferous pig... 435
Production of Steel..... 440
Problem 78.—The induction electric furnace... 442
Problem 79.—The electric "pig and ore" process 443
Problem 80.—Electrolytic refining; Burgess' process..... 446

APPENDIX: PROBLEMS FOR PRACTICE.....452–465
Problem 81.—Diameter of tuyeres for a blast furnace..... 452
Problem 82.—Blast furnace slag calculation..... 452
Problem 83.—Carbon burned before the tuyeres..... 453
Problem 84.—Calculation of blast furnace charge... 454
Problem 85.—Slag calculation for various slags..... 454
Problem 86.—Weight of flux needed..... 455
Problem 87.—Volume of blast, and cooling of same by expansion..... 456
Problem 88.—Output of a blast-furnace..... 456

PAGE

Problem 89.—Efficiency of the blowing engines.... 456
Problem 90.—Power producible from blast-furnace gases..... 457
Problem 91.—Proportion of gases required by hot-blast stoves..... 457
Problem 92.—Complete balance sheet of a blast furnace..... 458
Problem 93.—Working of a foundry cupola..... 460
Problem 94.—The Monell process in an open-hearth furnace..... 460
Problem 95.—Volume of blast required by a Bessemer converter..... 461
Problem 96.—Volume of blast received by a Bessemer converter..... 461
Problem 97.—Loss of weight of a Bessemer charge. 462
Problem 98.—Balance sheet of a complete Bessemer blow..... 462
Problem 99.—Lime needed in a basic Bessemer blow 464
Problem 100.—Power of blowing engines required for a converter..... 465
INDEX..... 466

CONTENTS TO PART III.

PAGE

CHAPTER I.—THE METALLURGY OF COPPER.....469–577

Roasting and Smelting of Copper Ores..... 469

The Roasting Operation..... 475

Problems 101–104.

Pyritic Smelting..... 483

Fundamental Principles..... 485

Theoretical Temperature at the Focus..... 486

Use of Auxiliary Coke..... 488

Rate of Smelting..... 489

Problems 105, 106.

Smelting of Copper ores..... 499

Reverberatory Smelting..... 501

Problems 107, 108.

"Bringing Forward" of Copper Matte..... 514

The Welsh Process..... 514

Problem 109.

"Blister Roasting" or Roasting-Smelting..... 523

"Bessemerizing" Copper Matte..... 525

Theoretical Temperature Rise..... 527

Problem 110.

The Electrometallurgy of Copper..... 534

Electrolytic Processes..... 536

Treatment of Ores by Electrolysis..... 536

Problem 111.

Electrolytic Treatment of Matte..... 539

Use of Matte as Anode..... 539

Problem 112.

Use of Matte as Cathode..... 545

Problem 113.

Extraction from Solutions..... 548

(1) Use of Iron Anodes..... 548

PAGE

Problems 114, 115.
(2) Use of Insoluble Anodes..... 551
Problems 116, 117, 118
Electrolytic Refining of Impure Copper..... 558
Energy Absorbed by Electrolyte..... 559
Problem 119.
Energy Lost in Contacts..... 562
Problem 120.
Energy Lost in Conductors..... 567
Problem 121.
Electric Smelting..... 572
Problem 122.

CHAPTER II.—THE METALLURGY OF LEAD.....578–604
The Volatility of Lead..... 583
Roasting of Lead Ores..... 586
Problem 123.
Reduction of Roasted Ore..... 591
Problem 124.
The Electrometallurgy of Lead..... 598
Problems 125, 126.

CHAPTER III.—THE METALLURGY OF SILVER AND GOLD.605–619
Electrolytic Refining of Silver Bullion..... 605
Problems 127, 128.
The Volatilization of Silver and Gold..... 614

CHAPTER IV.—THE METALLURGY OF ZINC.....620–657
Roasting of Sphalerite..... 620
Problems 129, 130.
Reduction of Zinc Oxide..... 627
Thermochemical Considerations..... 628
Heating up the Charge..... 628
Problem 131.
Distillation of the Charge..... 632
Problems 132, 133, 134.
Electric Smelting of Zinc Ores..... 637
Zinc Vapor..... 643

PAGE

Problem 135.
Condensation of Zinc and Mercury..... 649
Metallic Mist or Fume Vapor..... 656

CHAPTER V.—METALLURGY OF ALUMINIUM.....658–661
Electrolytic furnace reduction of alumina..... 658
INDEX..... 663

METALLURGICAL CALCULATIONS.

INTRODUCTION.

The making of calculations respecting the quantitative working of any process, furnace or piece of apparatus used in metallurgical operations is of the greatest importance for estimating the real efficiency of the process, for determining avenues of waste and possible lines of improvement, and for obtaining the best possible comprehension of the real principles of operation involved.

The possibility of making such calculations respecting any process, furnace or apparatus depends on skill in collecting such necessary data as can be obtained by observation or measurement, the insight or intuition to see the further use which can be made of said data when once obtained, and, finally on the possession of a working knowledge of the fundamental chemical, physical and mechanical principles involved in the calculations. The highest desideratum, all in all, however, is a plain analytical, common sense mind, capable of clear, logical thinking It is the writer's conviction that no study of details, or even observation of plants in actual operation, can supply the insight into metallurgical processes and principles, such as is gained by these calculations, in addition to the high grade of mental training involved.

Scope of the Treatise

Discussion of the chemical equation.
Weights and volumes of gases.
Correction of gas volumes for temperature and pressure.
Combustion of commercial fuels.
Heat of chemical combination; of combustion.
Theoretical flame temperatures:
    With pure oxygen.
    With ordinary air.

With diluted air: Farley's system.
With hot air and cold gas.
With hot air and hot gas.
Effect of excess air.
Calculation of furnace efficiencies.
Chimney draft.
Water gas.
Producer gas: Efficiency, effect of drying.
Mixed gas:
Use of steam in producers.
Increased efficiency.
Maximum steam permissible.
Transmission of heat through metals, brick, etc.
Regenerative gas furnace:
Proportioning of gas and air regenerators.
Efficiency of regenerators.
Heat balance sheet.
Theoretical temperatures under different conditions.
Gas engines:
Calculation of temperature in cylinder.
Efficiency; balance sheet.
Cupolas: Amount of blast required.
Efficiency of running.
Blast furnaces:
Balance sheet of materials.
Calculation of blast received.
Efficiency of blowing engines.
Power and dimensions of blowing engines.
Carbon consumed at tuyeres.
Effect of atmospheric changes.
Effect of the moisture in the blast.
Calculation of the temperature.
Effect of hot-blast.
Heat balance sheet of the furnace.
Power producible from the waste gases.
Hot-blast stoves: Theory of iron-pipe and fire-brick stoves.
Efficiency.
Bessemer Converters:
Blast required and time of operation
Balance sheet of materials.

Heating efficiency of various ingredients of bath.
Heat balance sheet.
Theoretical rise in temperature.
Conversion of copper matte.

Open-hearth Furnaces:
Pig and ore process; calculation of charge.
Heat evolved or absorbed in bath reactions.
Efficiency of furnaces; of furnaces and producers.
Heat balance sheet.

Pyritic smelting.

Electric furnaces:
Working temperatures.
Heat balance sheet.
Efficiency.

Electrolytic furnaces:
Absorption of heat in chemical decompositions.
Equilibrium of temperature attained.
Ampere and energy efficiency.

Electrolytic refining:
Calculation of plant and output
Power requirements; temperature of baths.
Ampere and energy efficiency.

Condensation of metallic vapors:
Principles involved.
Application to condensation of zinc and mercury.

CHAPTER I.

THE CHEMICAL EQUATION.

The calculation of the quantitative side of many metallurgical processes depends upon the correct understanding of chemical equations. Every chemical equation is capable of giving three most important sets of data concerning the process which it represents; its shows the relative weights of the reacting substances, their relative volumes, when in the gaseous state, and the surplus or deficit of energy involved in the reaction, when the heats of formation of the substances concerned are known.

Atomic Weights.

These are the basis of all quantitative chemical calculations. For metallurgical purposes we may use them in round numbers as:

Hydrogen	H	1	Arsenic	As	75
Lithium	Li	7	Selenium	Se	79
Beryllium	Be	9	Bromine	Br	80
Boron	B	11	Strontium	Sr	87
Carbon	C	12	Zirconium	Zr	90
Nitrogen	N	14	Columbium	Cb	94
Oxygen	O	16	Molybdenum	Mo	96
Fluorine	F	19	Palladium	Pd	106
Sodium	Na	23	Silver	Ag	108
Magnesium	Mg	24	Cadmium	Cd	112
Aluminium	Al	27	Tin	Sn	118
Silicon	Si	28	Antimony	Sb	120
Phosphorus	P	31	Tellurium	Te	126
Sulphur	S	32	Iodine	I	127
Chlorine	Cl	35.5	Barium	Ba	137
Potassium	K	39	Tantalum	Ta	183
Calcium	Ca	40	Tungsten	W	184

Titanium	Ti	48	Iridium	Ir	193
Vanadium	V	51	Platinum	Pt	195
Chromium	Cr	52	Gold	Au	197
Manganese	Mn	55	Mercury	Hg	200
Iron	Fe	56	Thallium	Tl	204
Nickel	Ni	58.5	Lead	Pb	207
Cobalt	Co	59	Bismuth	Bi	208
Copper	Cu	63.6	Thorium	Th	232
Zinc	Zn	65	Uranium	U	238

Relative Weights.

Writing any chemical equation between elements or their compounds, the relative weights concerned in the reaction are obtained directly from using these atomic weights, which are, themselves, of course, only relative. *E.g.*, the slagging of iron in Bessemerizing copper matte:

$$2FeS + 3O^2 + 2SiO^2 = 2(FeO.SiO^2) + 2SO^2$$
$$176 + 96 + 120 = 264 + 128$$

These relative weights may be called kilograms or tons, pounds, ounces or grains; whatever units of weight we may be working in. In most metallurgical work we use kilograms or pounds as the convenient weight units.

Relative Volumes of Gases.

Where gases are involved, the relative number of molecules of the gaseous substance concerned in the reaction stands for the relative volume of that gas concerned in the reaction. It is usual and convenient to designate these relative volumes by Roman numerals, placed above the formulæ. The following are some examples:

Complete combustion of carbon:

$$C + \overset{I}{O^2} = \overset{I}{CO^2}$$

Incomplete combustion of carbon:

$$2C + \overset{I}{O^2} = \overset{II}{2CO}$$

Combustion of marsh gas:

$$\overset{I}{CH_4} + \overset{II}{2O_2} = \overset{I}{CO_2} + \overset{II}{2H_2O}$$

Production of water gas:

$$C + H^2O = CO + H^2$$
$$\text{I} \quad \text{I} \quad \text{I}$$

In each case above, the volume of a solid or liquid cannot be stated, but the relative volumes of all the gases taking part in a reaction are derived simply from the number of molecules of each gas concerned. These relative volumes may be called so many cubic meters or liters, or cubic feet, or whatever measure is wanted or being used. In most metallurgical calculations it is convenient to use cubic meters or cubic feet.

Exact Weights and Exact Volumes.

If we specify or fix the weights used, as, for instance, so many kilograms of each substance as the numbers representing the relative weights, then we can, by using one constant factor, convert all the relative volumes into the real or absolute volumes corresponding to the weights used. If, for instance, we take the equation of the production of water gas:

$$\text{I} \quad \text{I} \quad \text{I}$$
$$C + H^2O = CO + H^2$$
$$12 + 18 = 28 + 2$$

With the relative weights written beneath and the relative volumes above, then if we fix the weights as kilograms, the relative volumes can be converted into actual volumes in cubic meters by multiplying by 22.22. A cubic meter of hydrogen gas (under standard conditions) weighs 0.09 kilogram, and thence 2 kilograms will have a volume of $2 \div 0.09 = 22.22$ cubic meters. But the relative volumes show that the CO and H^2O gas are the same in volume as the hydrogen, and it, therefore, follows that each Roman I stands for 22.22 cubic meters of gas, if the weights underneath are called kilograms. The consideration of these relations is very advantageous, because, by means of this factor (22.22) we pass at once from the weight of a gas to its volume; each molecule or molecular weight of a gas, in kilograms (or, briefly, each kilogram-molecule), represents 22.22 cubic meters of that gas.

The conversion from weight to volume is quite as simple using English measures; and, by a strange coincidence, the same factor can be used as in the metric system. The coin-

cidence alluded to is the fact (which the writer, as far as he can discover, was the first to notice) that there happens to be the same numerical relation between an ounce (av.) and a kilogram, as there is between a cubic foot and a cubic meter; in short, there are 35.26 ounces (av.) in a kilogram, and 35.31 cubic feet in a cubic meter. The difference is only one-seventh of one per cent., which can be ignored, and we can therefore say that if the relative weights in an equation are called ounces (av.), each molecule of gas in the equation represents 22.22 cubic feet.

Example.—The production of acetylene from calcium carbide:

$$\begin{array}{c} \overset{\text{I}}{} \\ CaC^2 + H^2O = CaO + C^2H^2 \\ 64 \ + \ 18 \ = \ 56 \ + \ 26 \end{array}$$

Interpreting by weights, and calling the relative weights ounces, we can call the I molecule of C^2H^2 gas 22.22 cubic feet, so that, theoretically, 64 ounces of pure carbide, acting on 18 ounces of water, produce 56 ounces of lime and 26 ounces of C^2H^2 gas, the volume of which is 22.22 cubic feet.

Weights and Volumes of Gases.

The weight of one cubic meter of dry air, under standard conditions (at 0° Centigrade and at a pressure of 760 millimeters of mercury), is 1.293 kilograms. The composition of air is:

	By Weight.	By Volume.
Oxygen.....	3	21
Nitrogen.....	10	80
or, in percentages,		
Oxygen.....	23.1	20.8
Nitrogen.....	76.9	79.2

While these may not represent the absolutely accurate average composition of dry air, yet the variations are such that the above simple ratios, 3 to 10 and 21 to 80, are close enough for all practical purposes in metallurgy.

The weight of one cubic foot of dry air is 1.293 ounces (av.).

The weight of one cubic meter of hydrogen gas, at standard conditions, is 0.09 kilogram (1 cubic foot, 0.09 ounces). The formula of hydrogen gas is H^2, is molecular weight 2; and since the densities of all gases are found experimentally to

be proportional to their molecular weights, it follows that the density of any gas referred to hydrogen is expressed numerically by one-half its molecular weight. But the weight of a cubic meter of gas is the weight of a cubic meter of hydrogen multiplied by the density of the gas referred to hydrogen; thus, is obtained the weight of a cubic meter of any gas whose formula is known. Examples follow:

Formula.	Molecular Weight.	Density Referred to Hydrogen.	Weight of 1 Cubic Meter.
Hydrogen.....H^2	2	1	0.09 kilos.
Water vapor.....H^2O	18	9	0.81 "
Nitrogen.....N^2	28	14	1.26 "
Oxygen.....O^2	32	16	1.44 "
Carbon monoxide...CO	28	14	1.26 "
Carbon dioxide.....CO^2	44	22	1.98 "
Marsh gas.....CH^4	16	8	0.72 "

Etc., etc.

In the case of water vapor, a particular explanation is necessary. It cannot exist under standard conditions, but condenses to liquid at 100° C. if under 760 millimeters pressure. It does exist at lower temperatures than 100°, but only under partial pressures of fractions of an atmosphere; thus, at a pressure of 1-50 atmosphere (when it forms 1-50 of a mixture of gases) it can exist uncondensed at ordinary temperatures (15° C. or 60° F.). The above weight for a cubic meter of water vapor (0.81 kilos. per cubic meter at standard conditions) is, therefore, only a hypothetical value, but it is extremely useful, because it enables us to calculate, by the principles to be explained further on, the weight of a cubic meter of water vapor under any conditions of temperature and pressure at which it is possible for it to exist.

Corrections for Temperature.

The volumes of all permanent gases increase uniformly for uniform increase of temperature, so that, starting with a given volume at 0° C., it is found that their volume increases 1/273 for every degree Centigrade rise in temperature. Thus, at 273° C., the volume is just double the volume at 0°. Stating this fact in another way, we may say that the gas acts as if it would have no volume at $-273°$ C., and would increase uniformly

in volume from this point up to all measurable temperatures, the increment being, for each degree, 1-273 of the volume which the gas has at 0° C. A still briefer statement is that the volume of a gas is proportional to its temperature above — 273° C., or to its absolute temperature—the latter being its temperature in C° + 273.

The converse of these principles is, that the density of a gas; that is, the weight of a unit volume, varies inversely as its absolute temperature.

In Fahrenheit degrees, we can say that a gas expands 1-490 (1-273 × 5-9) for every degree rise above 32° C.; or that the volume is proportional to the absolute temperatures, *i.e.*, to the F°. — 32 + 490 (= F.° + 458).

These principles are in constant use in metallurgical calculations. Thus, one kilogram of coal will need 8 cubic meters of air to burn it, at 0° and 760 millimeters pressure. What volume will that be at 30° C. and the same pressure? Since 30° C. is 30 + 273 = 303° absolute, the two temperatures will be 273 and 303, and the

$$\text{Volume at } 30° \text{ C.} = \text{volume at } 0° \text{ C.} \times \frac{303}{273}$$

It is always to be recommended to make such calculations in the above form; that is, to first put down the known volume, and then to multiply it by a fraction, the numerator and denominator of which are the two absolute temperatures. A moment's reflection will show which way the fraction must be written; if the new volume must be greater than the old, the value of the fraction must be greater than unity, the higher temperature must be in the numerator; if the fraction were inverted, we know that the result would be less than the starting volume instead of greater, which would be wrong.

Taking an example in Fahrenheit degrees: What is the volume under standard conditions of 175 cubic feet of gas measured at 90° F. and standard pressure (29.93 inches of mercury)? Since 32° F. is 490° absolute and 90° F. is 548° absolute, and the new volume must be *less* than the starting volume, we have

$$\text{Volume at } 32° \text{ F.} = 175 \times \frac{490}{548} = 156.5 \text{ cubic feet}$$

Corrections for Pressure.

The principle is that the volumes of a gas are inversely as the pressure upon it, so that doubling the pressure halves the volume, etc. Since the practical problems almost always present the pressure as two numbers, all that is necessary is to multiply the original volume by a fraction whose numerator and denominator are the two pressures concerned, and arranged with the numerator the larger or the smaller of the two numbers, according as to whether the final volume should be greater or less than the starting one. Putting the solution in this manner avoids the primary school method of making a proportion, which is so apt to be expressed upside down, and absolutely avoids error with the minimum exercise of brain power.

Examples.—What is the volume of 100 cubic meters of any gas, if the pressure is changed to 700 millimeters?

$$\text{Answer: } 100 \times \frac{760}{700} = 108.6 \text{ cubic meters.}$$

What is the volume at standard pressure of 150 cubic feet of gas measured at 28.50 inches of mercury?

$$\text{Answer: } 150 \times \frac{28.50}{29.93} = 142.8 \text{ cubic feet.}$$

Corrections for Temperature and Pressure.

These can be both allowed for, by simply correcting first for one, and then for the other. Actually, the simplest statement is to put down the original volume, then to multiply it by one fraction, which corrects for temperature, and again by another fraction correcting for pressure, thinking out carefully for each fraction the proper way of expressing it, *i.e.*, whether it should increase or decrease the volume.

Examples.—What does 100 cubic meters of air at standard conditions become at 50° C. and 780 millimeters pressure?

$$\text{Solution: } 100 \times \frac{50+273}{273} \times \frac{760}{780} = 115.3 \text{ cubic meters.}$$

What is the weight of one cubic meter of hydrogen at 1000°

C. and 250 millimeters pressure, its weight at standard conditions being 0.09 kilograms?

$$\text{Solution: } 0.09 \times \frac{273}{1000+273} \times \frac{250}{760} = 0.00637 \text{ kilograms.}$$

What weight of oxygen is in 1500 cubic feet of dry air at 100° F. and at 28.50 inches of mercury? (Refer to weight of air at standard conditions, and percentage composition.)

$$\text{Solution: } 1.293 \times \frac{3}{13} \times \frac{490}{558} \times \frac{28.50}{29.93} \times 1500 = 374 \text{ ounces.}$$

What is the weight of 50 cubic meters of water vapor at a temperature of 30° C. and a pressure of 31.6 millimeters?

$$\text{Solution: } 0.81 \times \frac{273}{303} \times \frac{31.6}{760} \times 50 = 1.517 \text{ kilograms.}$$

$$\text{or } 50 \times \frac{273}{303} \times \frac{31.6}{760} \times 0.81 = 1.517 \text{ kilograms.}$$

The first expression calculates the weight of a cubic meter of water vapor at the assumed conditions, and multiplies by 50; the second calculates the hypothetical volume of the 50 cubic meters if reduced to standard conditions, and multiplies by the hypothetical weight of a cubic meter at those conditions.

Problems Illustrating Preceding Principles.

Problem 1.

A bituminous coal contains on analysis:

Carbon	73.60	Moisture	0.60
Hydrogen	5.30	Ash	8.05
Nitrogen	1.70		
Sulphur	0.75		100.00
Oxygen	10.00		

It is powdered and blown into a cement kiln by a blast of air.

Required: 1. The volume of dry air, at 80° F. and 29 inches barometric pressure theoretically required for the perfect combustion of one pound of the coal.

2. The volume of the products of combustion, using no excess

of air, at 550° F. and 29 inches barometer, and their percentage, composition.

Solution: The reactions of the combustion are:

$$C + O^2 = CO^2 \qquad S + O^2 = SO^2$$
$$12 \quad 32 \quad 44 \qquad 32 \quad 32 \quad 64$$
$$2H^2 + O^2 = 2H^2O$$
$$4 \quad 32 \quad 36$$

Requirement (1):

The oxygen required for burning one pound of coal is:

Oxygen for carbon..... = $0.7360 \times 32/12$ = 1.963 pounds.
Oxygen for hydrogen.... = $0.0530 \times 32/4$ = 0.424 "
Oxygen for sulphur ..... = $0.0075 \times 32/32$ = 0.0075 "

Total required.....2.3945 "
Oxygen in coal.....0.1000 "

Oxygen to be supplied.....2.2945 "
Nitrogen accompanying.....7.6483 "

Air necessary.....9.9428 "
= 159.08 ounces (av.).

Volume of air necessary (standard conditions)

$$= \frac{159.08}{1.293} = 123.03 \text{ cubic feet.}$$

Volume of air necessary at 80° F. and 29 inches barometer =

$$123.03 \times \frac{80+458}{490} \times \frac{29.93}{29} = 139.4 \text{ cubic feet.} \qquad (1)$$

Requirement (2):

	Pounds.
The weight of CO^2 formed is.....$0.7360 + 1.963$ =	2.699
The weight of H^2O formed is.....$0.0530 + 0.424$ =	0.477
The weight of moisture is.....	0.006
The weight of SO^2 formed is.....$0.0075 + 0.0075$ =	0.015

The weight of nitrogen altogether is $7.6483 + 0.0170 = 7.6653$ pounds. Converting these weights into ounces, and dividing each by the weight of a cubic foot of each gas in ounces, we have the volume of these theoretical products at standard conditions:

Volume CO^2 = $2.699 \times 16 \div 198$ =
$43.184 \div 1.98$ = 21.80 cubic feet.
Volume H^2O = $0.483 \times 16 \div 0.81$ =
$7.728 \div 0.81$ = 9.54 " "
Volume SO^2 = $0.015 \times 16 \div 2.88$ =
$0.2400 \div 2.88$ = 0.08 " "
Volume N^2 = $7.665 \times 16 \div 1.26$ =
$122.645 \div 1.26$ = 97.34 " "
Total volume at standard conditions..... = 128.76 " "
Volume at 550° F. and 29 inches barometer =

$$128.76 \times \frac{550+458}{490} \times \frac{29.93}{29} = 273.4 \quad \text{" "}$$

The percentage composition by volume follows from the above volumes as:

CO^2	17.0 per cent.	N^2	75.5 per cent.
H^2O	7.4 "		
SO^2	0.1 "		100.00

Problem 2.

Natural gas in the Pittsburg district contains:

Marsh gas	CH^4	60.70 per cent.
Hydrogen	H^2	29.03 "
Ethane	C^2H^6	7.92 "
Olefiant gas	C^2H^4	0.98 "
Oxygen	O^2	0.78 "
Carbonous oxide	CO	0.58 "

Required:

(1) The volume of air necessary to burn it.
(2) The volume of the products of combustion.

Reactions:

$$CH^4 + 2O^2 = CO^2 + 2H^2O$$
$$2H^2 + O^2 = 2H^2O$$
$$2C^2H^6 + 7O^2 = 4CO^2 + 6H^2O$$
$$C^2H^4 + 3O^2 = 2CO^2 + 2H^2O$$
$$2CO + O^2 = 2CO^2$$

Solution:

Oxygen required for CH^4..... = 0.6070×2 = 1.2140 parts.
Oxygen required for H^2..... = $0.2903 \times \frac{1}{2}$ = 0.1451 "

Oxygen required for C^2H^6.... $= 0.0792 \times 7/2 = 0.2772$ parts.
Oxygen required for C^2H^4.... $= 0.0098 \times 3 = 0.0294$ "
Oxygen required for CO..... $= 0.0058 \times \frac{1}{2} = 0.0029$ "
1.6686 "
Deduct oxygen already present.....0.0078 "
Leaves oxygen to be supplied.....1.6608 "

Corresponding to air..... $\frac{1.6608}{0.208} = 7.985$ " (1)

Volumes of products of combustion:

	CO^2	H^2O	N^2	
From CH^4.....	0.6070	1.2140		
From H^2.....		0.2903		
From C^2H^6.....	0.1584	0.2376		
From C^2H^4.....	0.0196	0.0196		
From CO.....	0.0058			
From air.....			6.3242	
Total products.....	0.7908	1.7615	6.3242	(2)

The above solution is entirely in relative volumes, which may be all considered cubic feet or cubic meters, and are true for equal conditions of temperature and pressure.

Problem 3.

A Bessemer converter contains 10 metric tons of pig iron of the following composition:

Carbon.....	3.00 per cent.
Manganese.....	0.50 "
Silicon.....	1.50 "
Iron.....	95.00 "

On being blown, one-third the carbon burns to CO^2, the rest to CO; 5 per cent. of iron is oxidized, and no free oxygen escapes from the converter. Blast is assumed to be dry.

Requirements:

(1) What weight of oxygen is needed during the blow.

(2) How many cubic meters of air, at standard conditions, will be needed.

(3) What will be the average composition of the gases.

Reactions:

$C + O^2 = CO^2$			$Si + O^2 = SiO^2$		
12	32	44	28	32	60
$2C + O^2 = 2CO$			$2Fe + O^2 = 2FeO$		
24	32	56	112	32	144
$2Mn + O^2 = 2MnO$					
110	32	142			

Oxygen needed:

C to CO^2	100 kilos.	$\times 32/12$	= 266.7 kilos.
C to CO	200 "	$\times 32/24$	= 266.7 "
Mn to MnO	50 "	$\times 32/110$	= 14.5 "
Si to SiO^2	150 "	$\times 32/28$	= 171.4 "
Fe to FeO	500 "	$\times 32/112$	= 142.8 "
Total			862.1 " (1)
Nitrogen accompanying this			= 2873.7 "
Air needed			3735.8 "

$$\text{Volume of air} = \frac{3735.8}{1.293} = 2889.3 \text{ cubic meters} \quad (2)$$

Volume of products of combustion:

$$CO^2 = 100 + 266.7 = 366.7 \text{ kilos} = \frac{366.7}{1.98} = 185.2 \text{ cu. m.}$$

$$CO = 200 + 266.7 = 466.7 \text{ kilos} = \frac{466.7}{1.26} = 370.4 \text{ cu. m.}$$

$$N^2 = \frac{2873.7}{1.26} = 2280.7 \text{ "}$$

Total volume ..... 2836.3 "

Percentage composition by volume:

CO^2	6.5 per cent.
CO	13.1 "
N^2	80.4 "

CHAPTER II.

THE APPLICATIONS OF THERMOCHEMISTRY.

The ordinary interpretation of the chemical equation by weight gives us the quantitative relations governing the reactions of substances upon each other, when the reaction proceeds to a finish. Unfortunately, much chemical instruction, as given in our elementary schools, and even in some of the higher ones, stops with the consideration of the weight relations and does not proceed to those equally important relations, the energetics of chemical reactions. In most of the reactions which occur in practical metallurgy, the quantity of the combustible used, or, more broadly, the amount of energy in the form of heat or electrical energy, necessary for producing the reactions desired, is the controlling factor regulating the practicability or impracticability, the commercial success or failure, of the process.

The relative values of fuels, the manufacture and utilization of gas, the principles of the regenerative furnace, the Bessemer process, electric reduction, and a host of metallurgical processes, depend essentially on the realization and utilization of chemical energy, and the only way to become conversant with the amounts of energy involved or evolved in these operations is to understand thoroughly the thermochemistry of the reactions concerned.

Thermochemical Nomenclature

The heat evolved when compounds are formed from the elements (in a few cases heat is absorbed) is determined experimentally by the use of the calorimeter. This branch is sometimes called "chemical calorimetry;" it is practically a department of experimental physics. The data obtained give the heat evolved for the total change from the components at room temperature to the resulting products, at room tem-

perature (or very near to it), and may be expressed per unit of weight of either component or of the substance formed. Thus, if carbon is burned in a calorimeter to carbonic acid gas, CO^2, the heat evolved may be reported or expressed as

8100 gram calories per gram of carbon burnt.
Or, 3037 gram calories per gram of oxygen used.
Or, 2209 gram calories per gram of CO^2 formed.

Of these three methods of expressing the results, the first is the more often used, especially by the physicist.

The chemist, however, finds it often more convenient and logical to express these heats of combination per formula weight of the substances combining and of product formed. *E.g.*, In the case of CO^2, which contains 12 parts of carbon and 32 of oxygen in 44 of the gas, the chemist would write,

$$(C, O^2) = 97,200,$$

meaning thereby that when 12 grams of carbon is burnt by 32 grams of oxygen, forming 44 grams of carbon dioxide, there is evolved 97,200 gram-calories. These are the laboratory units; for practical purposes, we call the weights kilograms and the heat units kilogram-calories (gram-calories are abbreviated to " cal. "; kilogram-calories to " Cal."). Ostwald, in his thermochemical tables writes $(C, O^2) = 972$ K, where K represents a unit 100 times as large as a gram-calorie, if weights are taken as being grams. Berthelot writes $(C, O^2) = 97.2$, where the heat units are kilogram-calories, if the weights concerned are taken as grams. Both these methods of expression are liable to cause confusion; the writer prefers to follow the older thermochemists (Hess, Naumann) and to use the larger number, *e.g.*, 97,200, which then means gram-calories, if weights are taken in grams (laboratory units), and kilogram-calories, if weights are taken in kilograms (practical units).

If it is desired to work in " British Thermal Units " (1 B. T. U. is the heat needed to raise one pound of water one degree Fahrenheit), the weights represented by the formula may be called pounds, and then the expression is as follows:

$$(C, O^2) = [97,200 \times 9/5] = 174,960 \text{ B. T. U.}$$

The factor 9/5 is simply the relation of 1° C. to 1° F.; the

reasoning is, of course, that if the combustion of 12 kilograms of carbon evolves 97,200 kilogram calories, or would heat 97,200 kilograms of water 1° C., that the combustion of 12 pounds of carbon would heat 97,200 pounds of water 1° C., or 174,960 pounds 1° F. From the equation as thus expressed and interpreted, the heat of combination per pound of carbon burnt, or of oxygen used, or of product formed, may be found in B. T. U. by dividing 174,960 by 12, 32 or 44, respectively.

Since it is very inconvenient, as well as unscientific, to have the two unrelated heat units, with their resulting double sets of experimental data, I strongly recommend the use of the metric data and metric Centigrade heat unit. It is, however, sometimes convenient, when all the data of a problem are given in English weights, to use as the unit of heat the "pound —1° C.," or the heat required to raise the temperature of one pound of water 1° C. This may be called the "pound cal.," as distinguished from the B. T. U. The advantage of using it is that all the experimental data of the metric system units are at once transferable to the English weights. *E.g.*, (C, O^2) = 97,200 pound cal., if the weights concerned in the formula (12, 32, 44) are called pounds.

The thermochemist gives all his experimental data in the form above explained, and we will now give all the important thermochemical data known which are useful in metallurgical calculations, *the data being for the reactions beginning and ending at* 15° C. (60° F.):

INTRODUCTION TO THERMOCHEMICAL TABLES.

In the thermochemical tables following, the heats of formation or combination are given first for the molecular weights represented by the formulas. What these molecular weights are, can be found by adding up the atomic weights of the atoms represented in the formula. The atomic weight table on pages 1 and 2 supplies the necessary data. The formula given represents, thermochemically, the union of the constituent parts separated by commas, the whole reaction being enclosed in parentheses, to distinguish it from the ordinary chemical formula. Thus, while (Ca, O) represents the union of 40 parts of calcium with 16 parts of oxygen to form 56 parts of calcium oxide, and (Ca, Si, O_3) represents the combination of 40 parts of calcium with

28 parts of silicon and 48 parts of oxygen to form 116 parts of calcium silicate, (CaO, SiO_2) represents the combination of 56 parts of lime with 60 parts of silica to form 116 parts of calcium silicate.

In order to facilitate the use of these data in metallurgical calculations, the succeeding columns give the heat evolution *per unit weight* of the metal or base involved, of the acid element or acid radical involved, and of the compound formed. This will save much calculation, for while the heat evolution per formula weight is of prime use in discussing the heat energy of chemical reactions, the heats of combination per unit weight of constituents or of the product are most convenient in ordinary calculations.

The column headed "To Dilute Solution" gives the total heat evolution inclusive of the heat of solution in a large excess of water. The differences between corresponding columns under this heading and the heading "Anhydrous," are the heat of solution, per formula weight, per unit of base, of acid, or of compound.

The order in which the elements are arranged in each table is the order of their heats of combination with *unit weight* of the *acid* element or radical, which expresses the real order of affinity of the metals in each case. The order is given for the "Anhydrous" condition, because this is more frequently concerned in metallurgy than "To Dilute Solution." Theoretically, the order of arrangement "To Dilute Solution" is the more uniform and logical, besides being invariable, but it is less useful in metallurgy, except where dilute solutions are concerned.

In order that an estimate may be made of heats of formation so far undetermined, there is given at the end of the tables a list of the "Thermochemical Constants of the Elements" per chemical equivalent or per unit of valence with which they enter into combination. These are based on the known law that the heats of formation of salts *to dilute solution* are additive functions, being simply the sum of the thermochemical combining power of the basic element and that of the acid element or radical. Assuming arbitrarily that hydrogen has zero for its thermochemical constant, the constants for those elements can be calculated for which any thermochemical data, even a single heat of formation, exist. Thus, referring to the table, on page 38, 57,200 for Na means that 23 parts of sodium going into combina-

tion contributes 57,200 calories towards the heat of formation of the compound formed, *irrespective* of what it is combining with. Similarly, 39,400 for Cl means that 35.5 parts of chlorine going into combination contributes 39,400 calories towards the heat of formation of any chloride, *irrespective* of the element it is combining with. The sum of these, 96,600, is the heat of formation of (Na, Cl) to dilute solution. By means of the table of constants given, simple addition gives the heat of formation of a large number of salts, from their elements (taken from their usual physical condition at room temperature) *per chemical equivalent* of base and acid, or of compound, involved. This is not per formula weight, except for monovalent elements, but is per chemical equivalent weight; it must be multiplied by the valency of the base in the formula, that is, by the number of chemical equivalents represented by the formula, to get the heat of formation per formula weight. Thus, $\frac{1}{3}$Al 40,100 plus Cl 39,400 gives 79,500 as the heat of formation of $\frac{1}{3}$Al Cl_3; from which we have 238,500 as the heat of formation of Al Cl_3, per formula weight.

While this table has considerable uses, it does not give the heats of formation of anhydrous compounds; its values must be corrected by the heats of solution, where known, to give the values for the anhydrous condition. Yet, these are frequently corrections of a minor order, and leave the table highly useful for getting first approximations to undetermined thermochemical data. Names of some elements are introduced whose thermochemical constants are unknown, being placed, at a guess, in their most probable position in the table. All quantities are positive, except these indicated negative. The + exponent after a symbol represents one positive valence, the − exponent one negative valence. A more detailed explanation of the matter can be found in an article by the writer in the Trans. American Electrochemical Society, 1903, Vol. IV, page 142.

Heat of Formation of Oxides

Formula	Anhydrous				To Dilute Solution			
	Molecular	Per Unit Weight of			Molecular	Per Unit Weight of		
		Metal	Oxygen	Oxide		Metal	Oxygen	Oxide
(Th, O_2)	326,000	1,304	10,188	1,235				
(Mi$_2$, O_3)[1]	472,000	1,655	9,850	1,417				
(La_2, O_3)	444,700	1,602	9,265	1,364				
(Nd_2, O_3)	435,100	1,506	9,006	1,291				
(Mg, O)	143,400	5,975	8,963	3,585	148,800	6,200	9,300	3,720
(Pr_2, O_3)	412,400	1,467	8,592	1,297				
(Li_2, O	135,800	9,700	8,488	4,527	167,000	11,929	10,437	5,567
(Ba, O)	133,400	974	8,338	872	161,500	1,179	10,938	1,051
(Ca, O)	131,500	3,288	8,219	2,348	149,600	3,740	9,350	2,671
(Sr, O)	131,200	1,508	8,200	1,274	158,400	1,821	9,900	1,538
(Al_2, O_3)	392,600	7,270	8,179	3,849				
(V_2, O_3)	353,200	3,463	7,358	2,355				
(Ce, O_2)	224,600	1,603	7,019	1,306				
(Ti, O_2)	218,400	4,550	6,825	2,730				
(U_3, O_8)	845,200	1,184	6,603	1,004				
(V, O)	104,300	2,045	6,519	1,557				
(U, O_3)	303,900	1,277	6,341	1,063				
(Na_2, O)	100,400	2,183	6,275	1,620	155,900	3,389	9,744	2,515
(K_2, O)	98,200	1,259	6,138	1,045	165,200	2,118	10,325	1,758
(Si, O_2)	196,000	7,000	6,125	3,267				
(Mn, O)	90,900	1,653	5,681	1,280				
(B_2, O_3)	272,600	12,391	5,679	3,894	279,900	12,723	5,831	3,999
(V_2, O_5)	447,000	4,324	5,588	2,423				
(Zr, O_2)	177,500	1,972	5,547	1,455				
(Zn, O)	84,800	1,305	5,300	1,058				
(Mn_3, O_4)	328,000	1,988	5,125	1,434				
(Cr_2, O_3)	243,900	2,345	5,081	1,605				
(Li_2, O_2)	152,650	10,904	4,833	3,318	159,840	11,417	4,995	3,474
(P_2, O_5)	365,300	5,895	4,566	2,572	400,900	6,466	5,013	2,823
(Ba, O_2)	145,500	1,062	4,547	861				
(Mo, O_2)	142,800	1,488	4,463	1,116				
(Sn, O)	70,700	599	4,419	527				
(Sn, O_2)	141,300	1,197	4,416	942				
(CO, O) (gas)	68,040	2,430	4,253	1,546	73,940	2,641	4,621	1,680
(H_2, O) solid	70,400	35,200	4,400	3,911				
(H_2, O) liquid	69,000	34,500	4,313	3,833				
(H_2, O) gas	58,060	29,030	3,629	3,226				
(Fe_3, O_4)	270,800	1,612	4,231	1,167				
(Cd, O)	66,300	592	4,144	518				
(Fe, O)	65,700	1,173	4,106	913				
(W, O_2)	131,400	714	4,106	620				
(W, O_3)	196,300	1,067	4,089	846				
(Fe_2, O_3)	195,600	1,746	4,075	1,223				
(Co O)	64,100	1,086	4,006	855				
(Mn, O_2)	125,300	2,278	3,916	1,440				

[1] Mi = Mischmetal—a mixture of rare earth metals sold commercially, containing cerium, thorium, yttrium, etc.

HEAT OF FORMATION OF OXIDES. (*Continued*)

Formula	Anhydrous				To Dilute Solution			
	Molecular	Per Unit Weight of			Molecular	Per Unit Weight of		
		Metal	Oxygen	Oxide		Metal	Oxygen	Oxide
(Ni, O)	61,500	1,051	3,844	826				
(Na_2, O_2)	119,800	2,604	3,744	1,536				
(Mo, O_3)	175,000	1,823	3,646	1,215				
(Sb_2, O_3)	166,900	695	3,479	580				
(Sb_2, O_4)	209,800	874	3,278	690				
(As_2, O_3)	156,400	1,043	3,258	790	148,900	993	3,102	752
(Pb, O)	50,800	245	3,175	228				
(C, O_2)(gas)	97,200	8,100	3,038	2,209	103,100	8,592	3,222	2,343
(Cr, O_3)	140,000	2,692	2,917	1,400				
(Bi_2, O_3)	139,200	335	2,900	300				
(Sb_2, O_5)	231,200	963	2,890	723				
(As_2, O_5)	219,400	1,463	2,743	954	225,400	1,503	2,818	980
(Cu_2, O)	43,800	344	2,738	306				
(Tl_2, O)	42,800	105	2,675	101	39,700	97	2,481	94
(Te, O_2)	.....	.....	.....	.....	78,300	624	2,447	497
(Cu, O)	37,700	593	2,356	474				
(S, O_2)	69,260	2,196	2,196	1,098	77,600	2,425	2,425	1,213
(Pb, O_2)	63,400	306	1,981	265				
(S, O_3) (gas)	91,900	2,872	1,915	1,149	141,000	4,406	2,938	1,763
(Tl_2, O_3)	87,600	215	1,825	192				
(C, O) (gas)	29,160	2,430	1,823	1,041				
(H_2, O_2)	47,300	23,650	1,478	1,391				
(Hg_2, O)	22,200	56	1,388	53				
(Hg, O)	21,500	108	1,344	100				
(Pd, O)	21,000	198	1,313	172				
(Pt, O)	17,000	87	1,063	81				
(Ag_2, O)	7,000	32	438	30				
(Au_2, O_3)	−11,500	−29	−240	−26				

HEAT OF FORMATION OF HYDRATES

A. From the Elements

Formula and Reaction	Anhydrous		To Dilute Solution	
	Per Formula Weight	Per Unit Weight of Metal	Per Formula Weight	Per Unit Weight of Metal
(Li, O, H)	112,200	16,030	118,000	16,860
(Mg, O_2, H_2)	217,800	9,075		
(Sr, O_2, H_2)	217,300	2,498	227,400	2,614
(Ca, O_2, H_2)	215,600	5,390	219,500	5,488
(K, O, H)	104,600	2,682	117,100	3,003
(Na, O, H)	102,700	4,465	112,450	4,889
(Al, O_3, H_3)	301,300	11,160		
(N, H_4, O, H)	88,800	.....	90,000	5,294
(Zn, O_2, H_2)	151,100	2,325		
(H, O, H) solid	70,400			
(H, O, H) liquid	69,000			
(H, O, H) gas	58,060			
(Tl, O, H)	57,400	260	54,300	246
(Bi, O_3, H_3)	171,700	825		

HEAT OF FORMATION OF HYDRATES—*Continued*

A. From the Elements

Formula and Reaction	Anhydrous		To Dilute Solution	
	Per Formula Weight	Per Unit Weight of Metal	Per Formula Weight	Per Unit Weight of Metal
(Te, O_4, H_2)			166,740	1,323
(Te, O_3, H_2)	145,600	1,156		
(Se, O_3, H_2)			124,500	1,576
(Se, O_4, H_2)	128,220	1,623	145,020	1,836
(Tl, O_3, H_3)	78,700	386		

B. From Metal, Oxygen and Water

Formula and Reaction	Anhydrous			To Dilute Solution		
	Per Formula Weight	Per Unit Weight of Metal	Per Unit Weight of Oxygen	Per Formula Weight	Per Unit Weight of Metal	Per Unit Weight of Oxygen
(Li_2, O, H_2O)	155,400	11,100	9,710	167,000	11,930	10,440
(Mg, O, H_2O)	148,800	6,200	9,300			
(Sr, O, H_2O	148,300	1,705	9,280	158,400	1,822	9,900
(Ca, O, H_2O)	146,600	3,665	9,162	150,500	3,763	9,406
(K_2, O, H_2O)	140,200	1,797	8,762	165,200	2,118	10,325
(Na_2, O, H_2O)	136,400	2,965	8,525	155,900	3,389	9,744
($Al_2, O_3, 3H_2O$)	395,600	7,326	8,242			
(Zn, O, H_2O)	82,100	1,263	5,131			
(Tl_2, O, H_2O)	45,800	112	2,863	39,600	97	2,475
($Bi_2, O_3, 3H_2O$)	136,400	328	2,842			
(Te, O_2, H_2O)	76,600	6,079	2,394			
(Te, O_3, H_2O)				97,740	776	2,036
(Se, O_2, H_2O)				55,500	703	1,735
(Se, O_3, H_2O	59,220	750	1,234	76,020	962	1,583
($Tl_2, O_3, 3H_2O$)	86,400	212	1,800			

C. From Metallic Oxide and H_2O

Formula and Reaction	Anhydrous				To Dilute Solution			
	Per Formula Weight	Per Unit Weight of			Per Formula Weight	Per Unit Weight of		
		Metallic Oxide	H_2O	Hydrate		Metallic Oxide	Combined H_2O	Dissolved Hydrate
($Li_2 O, H_2O$)	19,600	653	1,089	408	31,200	1,040	1,733	650
(MgO, H_2O)	5,400	135	300	93				
(SrO, H_2O)	17,100	166	950	141	27,200	264	1,511	225
(CaO, H_2O)	15,100	270	839	204	19,000	339	1,056	257
(K_2O, H_2O)	42,000	447	2,333	375	67,000	713	3,722	598
(Na_2O, H_2O)	36,000	581	2,000	450	55,500	895	3,083	694
($N H_4)_2O, H^2O$								
($Al_2O_3, 3H_2O$)	3,000	30	56	19				
(ZnO, H_2O)	−2,700	−33	−150	−27				
(Tl_2O, H_2O)	3,000	7	167	7	−3,200	−7	−178	−7
($Bi_2O_3, 3H_2O$)	−2,800	−7	−52	−6				
($Tl_2O_3, 3H^2O$)	−1,200	−3	−22	−2				

HEAT OF FORMATION OF SULFIDES

Formula	Anhydrous				To Dilute Solution of			
	Per Formula Weight	Per Unit Weight of			Per Formula Weight	Per Unit Weight of		
		Metal	Sulfur	Sulfide		Metal	Sulfur	Sulfide
(Li_2, S)	.....	.....	.....	.....	115,400	8,243	3,606	2,509
(K_2, S)	103,500	1,327	3,234	941	113,500	1,455	3,547	10,319
(Ba, S)	102,900	751	3,216	609	109,800	802	3,431	474
(Sr, S)	99,300	1,141	3,103	835	106,700	1,225	3,334	897
(Na_2, S)	89,300	1,941	2,791	1,145	104,300	2,267	3,259	1,337
(Nd_2, S_3)	285,900	993	2,977	744				
(Ca, S)	94,300	2,358	2,947	1,310	100,600	2,515	3,144	1,397
(Mg, S)	79,400	3,308	2,481	1,418				
(Mn, S)	45,600	829	1,425	524				
(Zn, S)	43,000	662	1,344	443				
(Al_2, S_3)	126,400	2,341	1,316	843				
(N, H_5, S)	40,000	2,105	1,250	776	36,700	1,931	1,147	720
(Cd, S)	34,400	307	1,075	239				
(K, S_2)	59,300	1,521	927	576	59,700	1,531	933	579
(Na, S_2)	49,500	2,152	773	556	54,400	2,365	850	611
(B^2, S^3)	75,800	3,445	790	642				
(Fe, S)	24,000	428	750	273				
(Co, S)	21,900	371	685	241				
(Tl_2, S)	21,600	106	675	92				
(Cu_2, S)	20,300	160	634	127				
(Pb, S)	20,200	98	631	85				
(Si, S_2)	40,000	1,429	625	435				
(Ni, S)	19,500	333	609	215				
(Sb_2, S_3)	34,400	143	358	102				
(Hg, S)	10,600	53	331	46				
(Cu, S)	10,100	159	316	106				
(H_2, S)								
(gas)	4,800	2,400	150	141	9,500	4,750	297	279
(Ag_2, S)	3,000	14	94	12				
(C, S_2)								
(gas)	−25,400	−2,117	−397	−334				
(liquid)	−19,000	−1,583	−297	−250				
(I, S)	0	0	0	0				

Heat of Formation of Selenides

Formula	Anhydrous				To Dilute Solution			
	Per Formula Weight	Per Unit Weight of			Per Formula Weight	Per Unit Weight of		
		Metal	Selenium	Selenide		Metal	Selenium	Selenide
(Li_2, Se)	83,000	5,929	1,051	892	93,700	6,693	1,186	1,008
(K_2, Se)	79,600	1,021	1,008	507	87,900	1,127	1,113	560
(Ba, Se)	69,900	510	885	324				
(Sr, Se)	67,600	777	856	408				
(Na_2, Se)	60,900	1,324	720	487	78,600	1,709	995	629
(Ca, Se)	58,000	1,450	727	487				
(Zn, Se)	30,300	466	384	210				
(Cd, Se)	23,700	212	300	124				
(Mn, Se)	22,400	407	284	167				
(N, H_5, Se)	17,800	937	225	184	12,800	674	162	136
(Cu, Se)	17,300	272	219	114				
(Pb, Se)	17,000	82	215	59				
(Fe, Se)	15,200	262	192	111				
(Ni, Se)	14,700	251	186	107				
(Co, Se)	13,900	236	176	101				
(Tl_2, Se)	13,400	33	170	21				
(Cu_2, Se)	8,000	63	101	39				
(Hg, Se)	6,300	32	80	23				
(Ag_2, Se)	2,000	93	25	7				
(H_2, Se) (gas)	−25,100	−12,550	−318	−310	−15,800	−7,900	−200	−195
(N, Se)	−42,300	−3,021	−534	−455				

Heat of Formation of Tellurides

Formula	Anhydrous			
	Per Formula Weight	Per Unit Weight of		
		Metal	Tellurium	Telluride
(Zn, Te)	31,000	477	246	162
(Cd, Te)	16,600	148	132	70
(Co, Te)	13,000	220	103	70
(Fe, Te)	12,000	214	95	66
(Ni, Te)	11,600	198	92	63
(Tl_2, Te)	10,600	26	84	20
(Cu_2, Te)	8,200	64	65	32
(Pb, Te)	6,200	30	49	19
(H_2, Te) (gas)	−34,900	−17,450	−277	−272

HEAT OF FORMATION OF ARSENIDES

Formula	Per Formula Weight	Per Unit Weight of		
		Metal	Arsenic	Arseniide
(H_3, As) (gas)	−44,200	−14,733	−589	−567

HEAT OF FORMATION OF ANTIMONIDES

Formula	Per Formula Weight	Per Unit Weight of		
		Metal	Antimony	Antimonide
(H_3, Sb) (gas)	−86,800	−28,933	−723	−706

HEAT OF FORMATION OF PHOSPHIDES

Formula	Per Formula Weight	Per Unit Weight of		
		Metal	Phosphorus	Phosphide
(Mn_3, P_2)	70,900	430	1,144	312
(H_3, P) (gas)	4,900	1,633	158	144
(Fe, P)	±0	±0	±0	±0

HEAT OF FORMATION OF NITRIDES

Formula	Anhydrous				To Dilute Solution			
	Per Formula Weight	Per Unit Weight of			Per Formula Weight	Per Unit Weight of		
		Metal	Nitrogen	Nitride		Base	Acid	Compound
(Ba_3, N_2)	149,400	363	5,336	340				
(Mg_3, N_2)	119,700	1,662	4,275	1,197				
(Ca_3, N_2)	112,200	935	4,007	758				
(Li_3, N)	49,500	2,357	3,536	1,414				
(Al, N)	45,450	1,683	3,246	1,109				
(Li, N)	18,750	2,679	1,339	893				
(H_3, N) (gas)	12,200	4,067	871	718	21,000	7,000	1,500	1,235
(liquid)	16,600	5,533	1,186	976				
(P_3, N_5)	81,500	876	1,164	500				

Heat of Formation of Hydrides

Formula	Per Formula Weight	Per Unit Weight of			Per Fromula Weight	Per Unit Weight of		
		Metal	Hydrogen	Hydride		Base	Acid	Compound
(Ca, H_2)	46,200	1,155	23,100	1,100				
(Li, H)	21,600	3,086	21,600	2,700				
(Sr, H_2)	38,400	441	19,200	431				
(Ba, H_2)	37,500	274	18,750	271				
(Pt_{15}, H)	16,950	6	16,950	6				
(Pt_{10}, H)	14,200	7	14,200	7				
(P_{12}, H_6)	53,400	144	8,900	141				
(Pd_{15}, H)	4,600	3	4,600	3				
(P, H_3) (gas)	+4,900	158	+1,633	144				
(Si, H_4) (gas)	−6,700	−239	−1,675	−209				
(N_4, H_4)	−19,000	−339	−4,750	−317	−26,100	−466	−6,525	−435
(As, H_3)	−44,200	−589	−14,730	−567				
(Sb, H_3)	−86,800	−723	−28,930	−706				

Heat of Formation of Hydrocarbons

(From Amorphous Carbon, to Gas, Unless Otherwise Specified)

Formula and Reaction	Name	State	Per Formula Weight	Per Unit Weight of		
				Carbon	Hydrogen	Compound
(C, H_4)	Methane (Marsh gas)	Gas	+21,700	+1,808	+5,425	+1,356
(C_2, H_2)	Acetylene	Gas	−52,300	−2,179	−26,150	−2,016
(C_2, H_4)	Ethylene (olefiant gas)	Gas	−8,700	−363	−2,175	−311
(C_2, H_6)	Ethane (ethylene hydride)	Gas	+29,100	+1,213	+4,850	+970
(C_3, H_4)	Allylene	Gas	−44,000	−1,222	−11,000	−1,100
(C_3, H_6)	Propylene	Gas	−700	−22	−133	−19
(C_3, H_8)	Propane (propylene hydride)	Gas	+39,200	+1,089	+4,900	+891
(C_6, H_6)	Benzene	Gas	+7,200	+100	+1,200	+92
		Liquid	+14,400	+200	+2,400	+185
(C_7, H_8)	Toluol	Liquid	+21,900	+261	+2,738	+238
(C_{10}, H_8)	Naphthalene	Liquid	+9,100	+76	+1,138	+71
		Solid	+13,700	+114	+1,713	+107
(C_{10}, H_{16})	Turpentine	Gas	+23,800	+197	+1,488	+175
		Liquid	+33,200	+277	+2,075	+244
(C_{14}, H_{10})	Anthracene	Solid	−2,600	−16	−260	−15
(C, H_4, O)	Methyl alcohol (wood alcohol)	Gas	+56,000	4,667	14,000	1,750
		Liquid	+65,050	5,420	16,260	2,033
(C_2, H_6, O)	Ethyl alcohol (grain alcohol)	Gas	+64,200	2,675	10,700	1,396
		Liquid	+74,900	3,120	12,480	1,628
(C_3, H_6, O)	Acetone	Gas	+63,150	1,754	10,525	1,089
		Liquid	+71,300	1,980	11,880	1,229

Heat of Combustion of Hydrocarbons

Formula	Name	State	Per Formula Weight		Calories per M^3	Calories per Kg	B.T.U. per $ft.^3$	B.T.U. per lb.
			Calorimeter Value	Practical Value	Water formed not condensed			
CH_4	Methane	Gas	213,500	191,620	8,623	11,976	970	21,555
C_2H_2	Acetylene	Gas	315,700	304,760	13,714	11,722	1,543	21,000
C_2H_4	Ethylene	Gas	341,100	319,220	14,365	11,400	1,616	20,520
C_2H_6	Ethane	Gas	372,300	339,480	15,277	11,315	1,719	20,365
C_3H_4	Allylene	Gas	473,600	451,720	20,327	11,295	2,287	20,150
C_3H_6	Propylene	Gas	499,300	466,480	20,992	11,105	2,362	19,995
C_3H_8	Propane	Gas	528,400	484,640	21,812	11,015	2,464	19,825
C_6H_6	Benzene	Gas	783,000	750,180	33,758	9,618	3,798	17,312
		Liquid	775,800	742,980	.....	9,525	.....	17,145
C_7H_8	Toluol	Liquid	934,500	890,740	.....	9,682	.....	17,430
$C_{10}H_8$	Naphthalene	Liquid	1,238,900	1,195,150	.....	9,337	.....	16,805
		Solid	1,234,300	1,190,550	.....	9,300	.....	16,740
$C_{10}H_{16}$	Turpentine	Gas	1,500,200	1,412,680	63,570	10,385	7,152	18,695
		Liquid	1,490,800	1,403,280	.....	10,318	.....	18,570
$C_{14}H_{10}$	Anthracene	Solid	1,708,400	1,653,700	.....	9,290	.....	16,545
CH_4O	Methyl alcohol	Gas	179,200	157,320	7,079	4,919	786	8,854
		Liquid	170,150	148,270	.....	4,633	.....	8,340
C_2H_6O	Ethyl alcohol	Gas	337,200	304,380	13,700	6,617	1,541	11,910
		Liquid	326,500	293,680	.....	6,384	.....	11,490
C_3H_6O	Acetone	Gas	435,450	402,630	18,120	6,942	2,038	12,495
		Liquid	427,300	394,480	.....	6,801	.....	12,240

Heat of Formation of Carbides

Formula	Per Formula Weight	Per Unit Weight of		
		Metal	Carbon	Carbide
(Al_4, C_3)	232,000	2,148	6,445	1,815
(Si, C)	26,520	947	2,210	663
(Mn_3, C)	9,900	60	825	57
(Fe_3, C)	8,460	50	705	47
(Ca, C_2)	−7,250	181	302	113
(Na, C)	−4,400	191	367	126
(Li, C)	−5,750	821	479	303
(Ag, C)	−43,575	403	3,631	363
(N_2, C_2)	−73,000 (gas)	−2,607	−3,042	−1,404

Heat of Formation of Carbonates

A. From the Elements

Formula	Anhydrous		To Dilute Solution	
	Per Formula Weight	*Per Unit Weight of Metal*	*Per Formula Weight*	*Per Unit Weight of Metal*
(Ba, C, O_3)	286,300	2,090		
(K_2, C, O_3)	282,100	3,617	288,600	3,700
(Sr, C, O_3)	281,400	3,234		
(Ca, C, O_3)	273,850	6,846		
(Na_2, C, O_3)	273,700	5,950	279,300	6,072
(Mg, C, O_3)	269,900	11,245		
(Mn, C, O_3)	210,300	3,824		
(N, H_5, C, O_3)	208,600	10,980	202,300	10,640
(Zn, C, O_3)	197,500	3,038		
(Fe, C, O_3)	187,800	3,354		
(Cd, C, O_3)	183,200	1,636		
(Pb, C, O_3)	170,000	821		
(Cu, C, O_3)	146,100	2,301		
(Ag_2, C, O_3)	123,800	593		

B. From Metal, Oxygen and CO_2

Formula and Reaction	Anhydrous			To Dilute Solution		
	Per Formula Weight	*Per Unit Weight of*		*Per Formula Weight*	*Per Unit Weight of*	
		Metal	*Oxygen*		*Metal*	*Oxygen*
(Ba, O, CO_2)	189,100	1,380				
(K_2, O, CO_2)	184,900	2,370	.....	191,400	2,454	
(Sr, O, CO_2)	184,200	2,117				
(Ca, O, CO_2)	176,650	4,416				
(Na_2, O, CO_2)	176,500	3,837	.....	182,100	3,959	
(Mg, O, CO_2)	172,700	7,195				
(Mn, O, CO_2)	113,100	2,056				
(N, H_5, O, CO_2)	111,400	5,863	.....	105,100	5,532	
(Zn, O, CO_2)	100,300	1,543				
(Fe, O, CO_2)	90,600	1,618				
(Cd, O, CO_2)	86,000	768				
(Pb, O, CO_2)	72,800	352				
(Cu, O, CO_2)	48,900	770				
(Ag_2, O, CO_2)	26,600	123				

C. From Metallic Oxide and CO_2

Formula and Reaction	Anhydrous				To Dilute Solution			
	Per Formula Weight	Per Unit Weight of			Per Formula Weight	Per Unit Weight of		
		Metallic Oxide	CO_2	Carbonate		Metallic Oxide	CO_2	Carbonate
(BaO, CO_2)	55,700	364	1,266	282				
(K_2O, CO_2)	86,700	922	1,970	628	93,200	992	2,118	675
(SrO, CO_2)	53,000	515	1,205	361				
(CaO, CO_2)	45,150	806	1,026	451				
(Na_2O, CO_2)	76,100	1,219	1,718	713	81,700	1,318	1,857	771
(MgO, CO_2)	29,300	733	666	349				
(MnO, CO_2)	22,200	313	505	193				
(NH_3, O, CO_2)	22,600	646	514	286	16,300	466	370	206
(ZnO, CO_2)	15,500	191	352	124				
(FeO, CO_2)	24,900	346	566	215				
(CdO, CO_2)	19,700	154	448	115				
(PbO, CO_2)	22,000	99	500	83				
(CuO, CO_2)	11,200	140	255	91				
(Ag_2O, CO_2)	19,600	82	445	71				

Heat of Formation of Bicarbonates

A. From the Elements

Formula and Reaction	Anhydrous		To Dilute Solution	
	Per Formula Weight	Per Unit Weight of Metal	Per Formula Weight	Per Unit Weight of Metal
(K, H, C, O_3)	233,300	5,987	228,000	5,846
(Na, H, C, O_3)	227,000	9,870	222,700	9,683
(N, H_4, H, C, O_3)	205,300	.....	199,000	

B. From Metal, Oxygen, H_2O and CO_2

Formula and Reaction	Anhydrous				To Dilute Solution			
	Per Formula Weight	Per Unit Weight of			Per Formula Weight	Per Unit Weight of		
		Metal	CO_2			Metal	CO_2	Compound
(K_2, O, H_2O, $2CO_2$)	203,200	2,605	2,309	1,016	192,600	2,469	2,189	963
(Na_2, O, H_2O, $2CO_2$)	190,600	4,143	2,166	1,135	182,000	3,957	2,036	1,083

C. From Metallic Oxide, H_2O and CO_2

Formula	Anhydrous				To Dilute Solution			
	Per Formula Weight	Per Unit Weight of			Per Formula Weight	Per Unit Weight of		
		Metallic Oxide	CO_2	Compound		Metallic Oxide	CO_2	Compound
(K_2O, H_2O, $2CO_2$)	105,000	1,117	1,193	525	94,400	1,004	1,073	472
(Na_2O, H_2O, $2CO_2$)	90,200	1,961	1,025	537	81,600	1,774	927	486

Heat of Formation of Nitrates

A. From the Elements

	Anhydrous		To Dilute Solution	
	Per Formula Weight	*Per Unit Weight of Metal*	*Per Formula Weight*	*Per Unit Weight of Metal*
(K, N, O_3)	119,000	3,051	110,700	2,582
(Ba, N_2, O_6)	227,200	1,658	217,800	1,590
(Li, N, O_3)	111,610	15,945	111,910	15,985
(Na, N, O_3)	110,700	4,813	106,000	4,609
(Sr, N_2, O_6)	219,800	2,726	214,700	2,468
(Ca, N_2, O_6)	202,000	5,050	206,000	5,150
(Mg, N_2, O_6)	.....	.....	206,300	8,596
(Mn, N_2, O_6)	.....	.....	146,900	2,671
(Zn, N_2, O_6)	.....	.....	131,700	2,022
(Tl, N, O_3)	58,150	285	48,180	236
(Fe, N_2, O_6)	.....	.....	119,000	2,125
(Co, N_2, O_6)	.....	.....	115,720	1,961
(Ni, N_2, O_6)	.....	.....	113,230	1,936
(Pb, N_2, O_6)	105,400	509	98,200	474
(Cu, N_2, O_6)	.....	.....	82,230	1,295
(Fe, N_3, O_9)	.....	.....	157,150	2,806
(H, N, O_3) (gas)	34,400	34,400	48,800	48,800
(Hg, N, O_3)	.....	.....	28,900	145
(Hg, N_2, O_6	.....	.....	54,000	270
(Ag, N, O_3)	28,700	275	23,000	213

Heat of Formation of Nitrates

B. From Metallic Oxide and N_2O_5

Formula and Reaction	Anhydrous				To Dilute Solution			
	Per Formula Weight	*Per Unit Weight of*			*Per Formula Weight*	*Per Unit Weight of*		
		Metallic Oxide	N_2O_5	*Nitrate*		*Metallic Oxide*	N_2O_5	*Nitrate*
(K_2O, N_2O_5)	141,000	1,500	1,306	698	124,400	1,323	1,152	616
(BaO, N_2O_5)	92,600	605	857	354	83,200	544	770	319
(Li_2O, N_2O_5)	86,220	2,874	798	583	86,820	2,894	804	587
(Na_2O, N_2O_5)	119,800	1,932	1,109	705	110,400	1,781	1,022	649
(SrO, N_2O_5)	87,400	848	809	414	82,300	799	762	390
(CaO, N_2O_5)	69,300	1,238	642	423	73,300	1,309	679	447
($MgO. N_2O_5$)	.....	.....	.....	...	61,600	1,540	570	416
(MnO, N_2O_5)	.....	.....	.....	...	54,800	772	507	306
(ZnO, N_2O_5)	.....	.....	.....	...	45,700	564	423	242
(Tl_2O, N_2O_5)	72,300	171	669	136	52,360	124	485	98
(FeO, N_2O_5)	.....	.....	.....	...	52,100	724	482	274
(CoO, N_2O_5)	.....	.....	.....	...	50,420	672	467	276
(NiO, N_2O_5)	.....	.....	.....	...	50,530	678	468	277
(PbO, N_2O_5)	53,400	240	494	161	46,200	207	428	140
(CuO, N_2O_5)	.....	.....	.....	...	43,330	545	401	231
($Fe_2O_3, 3N_2O_5$)	.....	.....	.....	...	115,100	719	1,066	428
(H_2O, N_2O_5)	−1,400	−78	−13	−11	27,400	1,522	254	214
(Hg_2O, N_2O_5)	.....	.....	.....	...	34,400	827	319	656
(HgO, N_2O_5)	.....	.....	.....	...	31,300	145	290	97
(Ag_2O, N_2O_5)	49,200	212	456	145	37,800	163	350	111

Heat of Formation of Silicates

Anhydrous

A. From the Elements				B. From the Constituent Oxides				
Formula and Reaction	*Per Formula Weight*	*Per Unit Weight of*		*Formula and Reaction*	*Per Formula Weight*	*Per Unit Weight of*		
		Metal	*Silicate*			*Metallic Oxide*	*SiO_2*	*Silicate*
(Ba, Si, O_3)	344,100	2,512	1,615	(BaO, SiO_2)	14,700	96	245	69
(Ca, Si, O_3)	345,350	8,634	2,977	(CaO, SiO_2)	17,850	319	297	154
(Ca_2, Si, O_4)	487,300	6,091	2,833	($2CaO, SiO_2$)	28,300	253	472	165
(Ca_3, Si, O_5)	619,050	5,159	2,715	($3CaO, SiO_2$)	28,550	170	476	125
(Sr, Si, O_3)	345,100	3,967	2,117	(SrO, SiO_2)	17,900	174	298	110
(Al_2, Si, O_5)	576,600	10,678	3,559	(Al_2O_3, SiO_2)	−12,000	−118	−200	−74
(Al_2, Si_2, O_7)	799,500	14,806	3,601	($Al_2O_3, 2SiO_2$)	14,900	146	124	67
(Li_2, Si, O_3)	363,100	25,936	4,034	(Li_2O, SiO_2)	31,300	1,043	522	348
(Na_2, Si, O_3)	342,100	7,437	2,804	(Na_2O, SiO_2)	45,700	737	762	375
(Ca_3, Al_2, Si_2O_{10})	1,227,550	Ca 10,228 Al 22,732	3,147	($3CaO, Al_2O_3, 2SiO_2$)	48,450	CaO 288 Al_2O_3 475	303	113
(H_4, Al_2, Si_2, O_9)	959,420	17,767	2,680	($2H_2O, Al_2O_3, 2SiO_2$)	36,820	361	307	103
(Mn, Si, O_3)	292,300	5,315	2,231	(MnO, SiO_2)	5,400	76	90	41
(Fe, Si, O_3)	271,000	4,839	2,053	(FeO, SiO_2)	9,300	129	155	70
(Zn, Si, O_3)	283,280	4,569	2,053	(ZnO, SiO_2)	8,800	113	147	64
(Zn_2, Si, O_4)	341,840	2,630	1,540	($2ZnO, SiO_2$)	−23,760	−147	−396	−107
				FeO 71.0 per cent. SiO_2 29.0 per cent.	.....	153	376	109
				FeO 57.6 per cent. CaO 12.0 per cent. SiO_2 30.4 per cent.	.....	(FeO) 243 (CaO) 1,167 (Sum) 201	461	140
				FeO 40.3 per cent. CaO 28.0 per cent. SiO_2 31.7 per cent.	.....	(FeO) 479 (CaO) 689 (Sum) 283	609	193
				FeO 39.7 per cent. CaO 15.2 per cent. Al_2O_3 9.2 per cent.. SiO_2 35.5 per cent	.....	(FeO) 335 (CaO) 875 (Bases) 206	375	133

Heat of Formation of Sulfates

A. From the Elements

Formula	Anhydrous		To Dilute Solution	
	Per Formula Weight	*Per Unit Weight of Metal*	*Per Formula Weight*	*Per Unit Weight of Metal*
(K_2, S, O_4)	344,300	4,414	337,700	4,340
(Ba, S, O_4)	339,400	2,477		
(Li_2, S, O_4)	333,500	23,820	339,600	24,260
(Sr, S, O_4)	330,200	3,795		
(Na_2, S, O_4)	328,100	7,133	328,500	7,141
(Ca,S, O_4)	317,400	7,935	321,800	8,045
(Mg, S, O_4)	300,900	12,540	321,100	13,380
(Al_2, S_3, O_{12})	.....	.....	879,700	16,290
(N_2, H_8, S, O_4)	283,500	7,875	281,100	7,808
(Mn, S, O_4)	249,400	4,535	263,200	4,785
(Zn, S, O_4)	229,600	3,532	248,000	3,815
(Fe, S, O_4)	.....	.....	234,900	4,195
(Co, S, O_4)	.....	.....	228,900	3,880
(Ni, S, O_4)	.....	.....	228,700	3,919
(Fe_2, S_3, O_{12})	.....	.....	650,500	5,808
(Tl_2, S, O_4)	221,800	544	213,500	523
(Cd, S, O_4)	219,900	1,963	231,600	2,068
(Pb, S, O_4)	215,700	1,042	.....	.....
(H_2, S, O_4)	192,200	96,100	210,200	105,100
(Cu, S, O_4)	181,700	2,861	197,500	3,110
(Hg_2, S, O_4)	175,000	438	.....	.....
(Ag_2, S, O_4)	167,100	774	162,600	753
(Hg, S, O_4)	165,100	826		

Heat of Formation of Sulfates

B. From Metallic Oxide and SO_3

Formula and Reaction	Anhydrous				To Dilute Solution			
	Per Formula Weight	*Per Unit Weight of*			*Per Formula Weight*	*Per Unit Weight of*		
		Metallic Oxide	*SO_3*	*Sulfate*		*Metallic Oxide*	*SO_3*	*Sulfate*
(K_2O, SO_3)	154,200	1,640	1,928	886	147,600	1,570	1,845	848
(BaO, SO_3)	114,100	745	1,426	490	.....			
(Li_2O, SO_3)	105,800	3,527	1,322	962	111,900	3,730	1,399	1,017
(SrO, SO_3)	107,100	1,040	1,339	585				
(Na_2O, SO_3)	135,800	2,190	1,698	956	136,200	2,197	1,702	959
(CaO, SO_3)	94,000	1,679	1,175	692	98,400	1,757	1,230	723
(MgO, SO_3)	65,600	1,640	820	547	85,800	2,145	1,072	715
(Al_2O_3, $3SO_3$)	.....	.....	.....	...	211,400	2,072	881	618
(MnO, SO_3)	66,600	938	832	441	80,400	1,132	1,005	532
(ZnO, SO_3)	52,900	653	661	328	71,300	880	891	443
(FeO, SO_3)	.....	.....	.....	...	77,300	1,074	966	509
(CoO, SO_3)	.....	.....	.....	...	72,900	972	911	470
(NiO, SO_3)	.....	.....	.....	...	75,300	1,011	941	487
(Fe_2O_3, $3SO_3$)	.....	.....	.....	...	179,200	1,120	747	448
(Tl_2O, SO_3)	87,100	205	1,089	173	78,800	186	985	156
(CdO, SO_3)	61,700	482	759	297	73,400	573	918	353
(PbO, SO_3)	73,000	328	912	241				
(H_2O, SO_3)	31,300	1,739	391	319	49,300	2,739	616	503
(CuO, SO_3)	52,100	655	651	326	67,900	853	849	425
(Hg_2O, SO_3)	60,900	146	761	123				
(Ag_2O, SO_3)	68,200	294	852	219	63,700	275	796	204
(HgO, SO_3)	51,700	239	646	175				

HEAT OF FORMATION OF BI-SULFATES

Formula and Reaction	Anhydrous			To Dilute Solution		
	Per Formula Weight	Per Unit Weight of		Per Formula Weight	Per Unit Weight of	
		Metal	Bi-sulfate		Metal	Bi-sulfate
(K, H, S, O_4)	276,100	7,080	2,030	272,900	6,974	2,006
(Na, H, S, O_4)	269,100	11,700	2,243	268,300	11,665	2,236
(N, H_5, S, O_4)	244,600	13,588	2,127	245,100	13,617	2,131

HEAT OF FORMATION OF PHOSPHATES

Anhydrous

A. From the Elements			B. From Metallic Oxide and P_2O_5				
Formula and Reaction	Per Formula Weight	Per Unit Weight of Metal	Formula and Reaction	Per Formula Weight	Per Unit Weight of		
					Metallic Oxide	P_2O_5	Phosphate
(Ba_3, P_2, O_8)	951,700	2,316	(3BaO, P_2O_5)	186,200	406	1,311	310
(Sr_3, P_2, O_8)	945,000	7,130	(3SrO, P_2O_5)	186,100	602	1,311	413
(Ca_3, P_2, O_8)	919,200	7,660	(3CaO, P_2O_5)	159,400	949	1,123	514
(Mg_3, P, O_8)	910,600	12,647	(3MgO, P_2O_5)	115,100	959	811	439
(Na_3, P, O_4)	452,400	6,557	($3Na_2O$, P_2O_5)	238,300	1,281	1,678	727
(Mn_3, P_2, O_8)	737,500	4,470	(3MnO, P_2O_5)	99,500	467	701	280

HEAT OF FORMATION OF ARSENITES AND ARSENATES

A. From the Elements

Formula and Reaction	Anhydrous		To Dilute Solution	
	Per Formula Weight	Per Unit Weight of Metal	Per Formula Weight	Per Unit Weight of Metal
(Na, As, O_2)	.....	.....	158,050	6,872
(Na_3, As, O_4)	360,800	5,229	381,500	5,529
(K_3, As, O_4)	.....	.....	396,200	3,386
(Sr_3, As_2, O_8)	761,000	2,915		
(Ca_3, As_2, O_8)	732,800	6,107		
(Mg_3, As_2, O_8)	712,600	9,897		
(Ba_3, As_2, O_8)	629,200	1,531		

HEAT OF FORMATION OF TUNGSTATES

Anhydrous

A. From the Elements			B. From Metallic Oxide and WO_3				
Formula and Reaction	Per Formula Weight	Per Unit Weight of Metal	Formula and Reaction	Per Formula Weight	Per Unit Weight of		
					Metallic Oxide	WO_3	Tungstate
(Na_2, W, O_4)	391,400	8,509	(Na_2O, WO_3)	94,700	1,527	408	322

B. From Metallic Oxide and As_2O_3 or As_2O_5

Formula and Reaction	Anhydrous				To Dilute Solution			
	Per Formula Weight	Per Unit Weight of			Per Formula Weight	Per Unit Weight of		
		Metallic Oxide	As_2O_3 or As_2O_5	Compound		Metallic Oxide	As_2O_3 or As_2O_5	Compound
(Na_2O, As_2O_3)	.....	.....	...	...	59,300	9,565	300	227
($3Na_2O$, As_2O_5)	201,000	1,081	874	483	242,400	1,303	1,054	583
($3K_2O$, As_2O_5)	.....	.....	...	...	278,400	987	1,210	544
($3SrO$, As_2O_5)	148,000	567	643	302				
($3CaO$, As_2O_5)	118,900	708	502	299				
($3MgO$, As_2O_5)	63,000	525	274	151				
($3Ba_2O$, As_2O_5)	9,600	21	42	14				

HEAT OF FORMATION OF BORATES. *A. From the Elements*

Formula and Reaction	Anhydrous		To Dilute Solution	
	Per Formula Weight	Per Unit Weight of Metal	Per Formula Weight	Per Unit Weight of Metal
(Na_2, B_4, O_7)	748,100	16,263	758,300	16,485

B. From Metallic Oxide and B_2O_3

Formula and Reaction	Anhydrous				To Dilute Solution			
	Per Formula Weight	Per Unit Weight of			Per Formula Weight	Per Unit Weight of		
		Metallic Oxide	B_2O_3	Borate		Metallic Oxide	B_2O_3	Borate
(Na_2O, $2B_2O_3$)	102,500	1,653	732	507	112,700	1,818	805	558

HEAT OF FORMATION OF MOLYBDATES. *Anhydrous*

A. From the Elements			B. From Metallic Oxide and MoO_3				
Formula and Reaction	Per Formula Weight	Per Unit Weight of Metal	Formula and Reaction	Per Formula Weight	Per Unit Weight of		
					Metallic Oxide	MoO_3	Molybdate
(Na_2, Mo, O_4)	363,800	7,909	(Na_2O, MoO_3)	88,400	1,426	612	429

HEAT OF FORMATION OF TITANATES. *Anhydrous*

A. From the Elements			B. From Metallic Oxide and TiO_2				
Formula and Reaction	Per Formula Weight	Per Unit Weight of Metal	Formula and Reaction	Per Formula Weight	Per Unit Weight of		
					Metallic Oxide	TiO_2	Titanate
(Na_2, Ti, O_3)	388,500	8,446	(Na_2O, TiO_2)	69,700	1,124	871	491

Heat of Formation of Manganates and Per-Manganates

Anhydrous

A. From the Elements			B. From Metallic Oxide and Mn_2O_7				
Formula and Reaction	*Per Formula Weight*	*Per Unit Weight of Metal*	*Formula and Reaction*	*Per Formula Weight*	*Per Unit Weight of*		
					Metallic Oxide	*Mn_2O_3 Mn_2O_7*	*Compound*
(Na_2, Mn, O_4)	269,400	5,857	(Na_2O, MnO_3)				
(K, Mn, O_4)	200,050	5,129	(K_2O, Mn_2O_7)				

Heat of Formation of Aluminates

Anhydrous

A. From the Elements			B. From Metallic Oxide and Al_2O_3				
Formula and Reaction	*Per Formula Weight*	*Per Unit Weight of Metal*	*Formula and Reaction*	*Per Formula Weight*	*Per Unit Weight of*		
					Metallic Oxide	*Al_2O_3*	*Aluminate*
(Na, Al, O_2)	533,000	11,587	(Na_2O, Al_2O_3)	40,000	645	394	244
(Ca, Al_2, O_4)	524,550	13,114	(CaO, Al_2O_3)	450	8	4	3
(Ca_2, Al_2, O_5)	658,900	8,236	(2CaO, Al_2O_3)	3,300	29	32	15
(Ca_3, Al_2, O_6)	780,050	6,500	(3CaO, Al_2O_3)	−7,050	−42	−69	−26

Heat of Formation of Cyanides

	Anhydrous				To Dilute Solution			
Formula and Reaction	*Per Formula Weight*	*Per Unit Weight of*			*Per Formula Weight*	*Per Unit Weight of*		
		Metal	*CN*	*Cyanide*		*Metal*	*CN*	*Cyanide*
(Ca, C_2, N_2)	.....	.....	.....	.....	41,650	1,041	801	453
(K, C, N)	33,450	858	1,287	515	30,250	776	1,163	465
(Na, C, N)	25,950	1,128	998	530	25,450	1,107	979	519
(Sr, C_2, N_2)	.....	.....	.....	.....	47,000	540	904	338
(Ba, C_2, N_2)	48,300	353	929	256				
(Ca, C_2, N_2)	.....	.....	.....	.....	41,650	1,041	801	453
(Mg, C_2, N_2)	.....	.....	.....	.....	34,000	1,417	654	447
(Ni, C_2, N_2)	−23,400	−400	−450	−212				
(Zn, C_2, N_2)	−24,550	−378	−472	−210				
(Fe_7, C_{18}, N_{18})	−256,700	−655	−549	−298				
(Cd, C_2, N_2)	−31,850	−284	−612	−194				
(Cu, C, N)	−20,375	−320	−784	−227				
(Pd, C_2, N_2)	−49,250 (gas)	−465	−947	−312				
(H, C, N)	−27,150	−27,150	−1,044	−1,006	−21,050	−21,050	−810	−781
(Hg, C_2, N_2)	−59,150	−296	−1,137	−235				
(Ag, C, N)	−34,000	−315	−1,308	−254				

Heat of Formation of Cyanates

A. From the Elements

Formula and Reaction	Anhydrous			To Dilute Solution		
	Per Formula Weight	Per Unit Weight of		Per Formula Weight	Per Unit Weight of	
		Metal	Cyanate		Metal	Cyanate
(K, C, N, O)	105,850	2,714	1,307	100,650	2,581	1,242
(Na, C, N, O)	105,050	4,567	1,616	100,250	4,359	1,542
(Ag, C, N, O)	26,450	245	176			
(Hg, C_2, N_2, O_2)	−62,900	−315	−221			

B. From Cyanide and Oxygen

Formula and Reaction	Anhydrous				To Dilute Solution			
	Per Formula Weight	Per Unit Weight of			Per Formula Weight	Per Unit Weight of		
		Cyanide	Oxygen	Cyanate		Cyanide	Oxygen	Cyanate
(KCN, O)	72,400	1,115	4,525	894	67,200	1,034	4,200	830
(NaCN, O)	79,100	1,614	4,944	1,217	74,300	1,516	4,644	1,143
(AgCN, O)	60,450	451	3,781	403				
(HgC_2N_2, O_2)	−3,750	−15	−117	−13				

Heat of Formation of Metallo-cyanides

A. From the Elements

Formula and Reaction	Anhydrous				To Dilute Solution			
	Per Formula Weight	Per Unit Weight of			Per Formula Weight	Per Unit Weight of		
		Metal	CN	Cyanide		Metal	CN	Cyanide
(K_4, Fe, C_6, N_6)	157,300	1,007	1,007	428	145,300	931	931	395
(H_4, Fe, C_6, N_6)	−102,000	−25,500	−652	−472	−101,500	−25,375	−650	−470
(K_3, Fe, C_6, N_6)	129,600	1,108	831	394	100,800	862	647	307
(H_3, Fe, C_6, N_6)	.....	.....	.....	.....	−127,400	−42,467	817	593
(K, Ag, C_2, N_2)	13,700	351	264	69	5,350	137	103	27

B. From the Constituent Cyanides

Formula and Reaction	Anhydrous				To Dilute Solution			
	Per Formula Weight	Per Unit Weight of			Per Formula Weight	Per Unit Weight of		
		Cyanide I	Cyanide II	Compound		Cyanide I	Cyanide II	Compound
(KCN, AgCN)	−86,100	−1,325	−642	−433	−94,450	−1,452	−704	−474

HEAT OF FORMATION OF AMALGAMS

Formula and Reaction	To Formula Given			
	Per Formula Weight	Per Unit Weight of		
		Mercury	Metal	Amalgam
(Hg, Na)	10,300	52	448	46
(Hg_2, Na)	17,800	45	774	42
(Hg_4, Na)	20,000	25	870	24
(Hg_6, Na)	21,900	18	952	18
(Hg_x, Na)	19,000	.....	826	.....
(Hg_2, K)	20,000	50	513	46
(Hg_4, K)	29,700	37	762	35
(Hg_9, K)	33,000	18	846	18
(Hg_{12}, K)	34,600	14	887	14
(Hg_x, K)	25,600	.....	656	.....
(Hg_x, Ag)	2,470	.....	23	.....
(Hg_x, Au)	2,580	.....	13	.....
($Hg_{3.41}$, Zn) 8.7% Zn	−1,345	−2	−21	−1.8
($Hg_{0.94}$, Zn 25.9% Zn	−703	−3.8	−11	−2.8

HEAT OF FORMATION OF ALLOYS

Formula or Composition	To Formula or Composition Given				Percentage Composition			
	Per Formula Given	Per Unit Weight of			Metal I		Metal II	
		Metal I	Metal II	Alloy		Per Cent.		Per Cent.
(Cu, Zn_2)	10,143	160	78	52	Cu	32.8	Zn	67.2
(Cu, Zn)	5,783	91	89	45	Cu	49.4	Zn	50.6
(Cu_3, Al)	26,910	141	997	124	Cu	87.6	Al	12.4
(Cu_2, Al)	21,278	167	788	138	Cu	82.5	Al	17.5
(Cu_3, Al_2)	17,395	91	322	71	Cu	77.9	Al	22.1
(Cu, Al)	1,887	30	70	21	Cu	70.2	Al	29.8
(Cu_2, Al_3)	10,196	80	126	49	Cu	61.1	Al	38.9
(Cu, Al_2)	31,900	502	591	271	Cu	54.0	Al	46.0
(Na_2, K) (liquid)	−2,930	−64	−75	−34	Na	54.1	K	45.9
(Na, K_2) (liquid)	1,940	84	25	19	Na	22.77	K	77.23
(Na, K_3) (liquid)	1,160	50	10	8	Na	16.43	K	83.57
(Pb_{19}, Zn)	23,188	6	357	5.8	Pb	98.4	Zn	1.6
(Pb, Zn)	952	4.6	15	+3.5	Pb	76.1	Zn	23.9
($Pb_{1.26}$, Bi)	−1,782	−6.9	−8.6	−3.8	Pb	55.6	Bi	44.4
($Sn_{6.1}$, Zn)	−4,789	−6.6	−74	−6.1	Sn	91.7	Zn	8.3
(Pb, $Sn_{15.7}$)	−8,034	−39	−4.3	−3.9	Pb	10.0	Sn	90.0
(Pb, $Sn_{3.6}$)	−1,028	−5.0	−3.1	−1.9	Pb	38.2	Sn	61.8
($Pb_{2.1}$, Sn)	450	1.0	3.5	0.8	Pb	79.0	Sn	21.0
($Pb_{19.8}$, Sn)	2,594	1.2	22	1.1	Pb	95.0	Sn	5.0
(Pb_{28}, Sn)	5,914	1.0	50	1.0	Pb	98.0	Sn	2.0
(Mg, Zn_2)	24,900	1,038	192	162	Mg	15.6	Zn	84.4
(Mg_4, Al_3)	164,800	1,717	204	93	Mg	54.2	Al	45.8
(Mg, Cd)	17,700	738	158	130	Mg	17.6	Cd	82.4
(Na, Cd_2)	30,800	1,339	137	125	Na	9.3	Cd	90.7
(Na, Cd_4)	60,600	2,635	108	104	Na	3.9	Cd	96.1
(Ca, Zn_4)	55,600	1,390	214	185	Ca	13.3	Zn	86.7
(Ca, Zn_{10})	199,100	4,978	306	29	Ca	5.8	Zn	94.2
(Cu_2, Cd_3)	47,700	376	142	103	Cu	27.4	Cd	72.6

THERMOCHEMICAL CONSTANTS OF BASES TO DILUTE SOLUTION.*

(*Per Chemical Equivalent of Base.*)

*For explanation of nature and use of these tables, see page 16.

Caesium	Cs^{+}	+81,240
Rubidium	Rb^{+}	76,265
Lithium	Li^{+}	62,900
Potassium	K^{+}	61,900
Beryllium (Glucinum)	$\frac{1}{2}Be^{++}$	60,350
Barium	$\frac{1}{2}Ba^{++}$	59,950
Thorium	$\frac{1}{4}Th^{++++}$	.....
Strontium	$\frac{1}{2}Sr^{++}$	58,700
Sodium	Na^{+}	57,200
Lanthanum	$\frac{1}{3}La^{+++}$	.....
Neodymium	$\frac{1}{3}Nd^{+++}$	55,600
Calcium	$\frac{1}{2}Ca^{++}$	54,400
Praesodymium	$\frac{1}{3}Pr^{+++}$	.....
Magnesium	$\frac{1}{2}Mg^{++}$	54,300
Aluminium	$\frac{1}{3}Al^{+++}$	40,100
Ammonium (from the elements)	$(N, H_4)^{+}$	33,400
Vanadium	$\frac{1}{3}V^{+++}$	.....
Cerium	$\frac{1}{4}Ce^{++++}$	.....
Titanium	$\frac{1}{4}Ti^{++++}$	.....
Uranium	$\frac{1}{5}U^{+++++}$	.....
Vanadium	$\frac{1}{2}V^{++}$	.....
Vanadium	$\frac{1}{6}V^{++++++}$	.....
Silicon	$\frac{1}{4}Si^{++++}$	.....
Boron	$\frac{1}{3}B^{+++}$	.....
Vanadium	$\frac{1}{5}V^{+++++}$	.....
Zirconium	$\frac{1}{4}Zr^{++++}$	.....
Manganese	$\frac{1}{2}Mn^{++}$	24,900
Zinc	$\frac{1}{2}Zn^{++}$	17,200
Chromium	$\frac{1}{3}Cr^{+++}$	.....
Phosphorus	$\frac{1}{5}P^{+++++}$	.....
Lithium (per-salts)	$\frac{1}{2}Li^{++}$	.....
Barium (per-salts)	$\frac{1}{4}Ba^{++++}$	.....
Iron (ferrous)	$\frac{1}{2}Fe^{++}$	10,900
Tungsten (Wolfram)	$\frac{1}{4}W^{++++}$	.....
Tungsten (Wolfram)	$\frac{1}{6}W^{++++++}$	.....
Cadmium	$\frac{1}{2}Cd^{++}$	9,000
Cobalt	$\frac{1}{2}Co^{++}$	8,200
Manganese	$\frac{1}{4}Mn^{++++}$	.....
Sodium (per-salts)	$\frac{1}{2}Na^{++}$	.....
Nickel	$\frac{1}{2}Ni^{++}$	7,700
Antimony	$\frac{1}{3}Sb^{+++}$	.....
Arsenic	$\frac{1}{3}As^{+++}$	.....
Sulfur	$\frac{1}{6}S^{++++++}$	2,800

Iron (ferric)	$\frac{1}{3}Fe^{+++}$	27,30
Tin (stannous)	$\frac{1}{2}Sn^{++}$	1,900
Tin (stannic)	$\frac{1}{4}Sn^{++++}$	.....
Lead	$\frac{1}{2}Pb^{++}$	400
Carbon	$\frac{1}{4}C^{++++}$	.....
Chromium	$\frac{1}{6}Cr^{++++++}$	.....
Bismuth	$\frac{1}{3}Bi^{+++}$	.....
Antimony	$\frac{1}{5}Sb^{+++++}$	.....
Arsenic	$\frac{1}{5}As^{+++++}$	.....
Copper (cuprous)	Cu^{+}	.....
Hydrogen	H^{+}	±0
Tellurium	Te^{+}	−900
Tellurium	$\frac{1}{4}Te^{++++}$	.....
Sulfur	$\frac{1}{4}S^{++++}$	−1,300
Selenium	$\frac{1}{2}Se^{++}$	.....
Selenium	$\frac{1}{3}Se^{+++}$	.....
Tellurium	$\frac{1}{2}Te^{++}$	.....
Copper (cupric)	$\frac{1}{2}Cu^{++}$	−7,900
Lead (per-salts)	$\frac{1}{4}Pb^{++++}$	.....
Thallium	$\frac{1}{3}Tl^{+++}$	.....
Carbon	$\frac{1}{2}C^{++}$	.....
Hydrogen (per-salts)	$\frac{1}{2}H^{++}$	.....
Mercury (mercurous)	Hg^{+}	.....
Palladium	$\frac{1}{2}Pd^{++}$	.....
Mercury (mercuric)	$\frac{1}{2}Hg^{++}$	−14,250
Platinum	$\frac{1}{4}Pt^{++++}$	−19,450
Silver	Ag^{+}	−25,300
Gold (auric)	$\frac{1}{3}Au^{+++}$	−30,300
Gold (aurous)	Au^{+}	.....

Thermochemical Constants of Acids to Dilute Solution

(*Per Chemical Equivalent of Acid Element or Radical*)

Elements

Fluorine	F^{-}	52,900
Chlorine	Cl^{-}	39,400
Bromine	Br^{-}	27,500
Oxygen	$\frac{1}{2}O^{--}$	20,700
Iodine	I^{-}	13,200
Sulfur	$\frac{1}{2}S^{--}$	−5,100
Selenium	$\frac{1}{2}Se^{--}$	−17,900
Tellurium	$\frac{1}{2}Te^{--}$	.....

Acid Radicals (*from the elements*)

Hydrate	$(O, H)^{-}$	55,200
Sulf-hydrate	$(S, H)^{-}$	3,400

Selen-hydrate	$(Se, H)^-$	19,100
Hypochlorite	$(Cl, O)^-$	27,500
Chlorate	$(Cl, O_3)^-$	21,900
Per-chlorate	$(Cl, O_4)^-$	39,400
Hypobromite	$(Br, O)^-$	22,800
Bromate	$(Br, O_3)^-$	6,700
Iodate	$(I, O_3)^-$	60,470
Per-iodate	$(I, O_4)^-$	48,070
Hypo-sulfite	$\frac{1}{2}(S_2, O_3)^{--}$	71,750
Sulfite	$\frac{1}{2}(S, O_3)^{--}$	75,100
Bi-sulfite	$(H, S, O_3)^-$	149,400
Pyro-sulfite	$\frac{1}{2}(S_2, O_5)^{--}$	115,200
Sulfate	$\frac{1}{2}(S, O_4)^{--}$	107,000
Bi-sulfate	$(H, S, O_4)^-$	211,100
Per-sulfate	$\frac{1}{2}(S_2, O_8)^{--}$	158,100
Di-thionate	$\frac{1}{2}(S_2, O_6)^{--}$	138,350
Tri-thionate	$\frac{1}{2}(S_3, O_6)^{--}$	136,500
Tetra-thionate	$\frac{1}{2}(S_4, O_6)^{--}$	130,600
Penta-thionate	$\frac{1}{2}(S_5, O_6)^{--}$	133,100
Selenite	$\frac{1}{2}(Se, O_3)^{--}$	60,050
Selenate	$\frac{1}{2}(Se, O_4)^{--}$	72,800
Hypo-nitrite	$(N, O)^-$	−3,800
Nitrite	$(N, O_2)^-$	27,000
Nitrate	$(N, O_3)^-$	48,800
Phosphate	$\frac{1}{3}(P, O_4)^{---}$	99,300
Mono-H-Phosphate	$\frac{1}{2}(H, P, O_4)^{--}$	152,750
Di-H-Phosphate	$(H_2, P, O_4)^-$	307,700
Arsenite	$\frac{1}{2}(As_2, O_4)^{--}$	102,150
Arsenate	$\frac{1}{3}(As, O_4)^{---}$	70,200
Mono-H-Arsenate	$\frac{1}{2}(H, As, O_4)^{--}$	108,050
Di-H-Arsenate	$(H_2, As, O_4)^-$	217,200
Cyanide	$(C, N)^-$	−34,900
Cyanate	$(C, N, O)^-$	37,100
Sulfo-cyanate	$(C, N, S)^-$	−18.100
Ferro-cyanide	$\frac{1}{4}(Fe, C_6, N_6)^{----}$	−25,600
Ferri-cyanide	$\frac{1}{3}(Fe, C_6, N_6)^{---}$	−52,800
Carbonate	$\frac{1}{2}(C, O_3)^{--}$	82,450
Bi-carbonate	$(H, C, O_3)^-$	169,100
Formate	$(C, H, O_2)^-$	104,600
Acetate	$(C_2, H_3, O_2)^-$	120,500
Oxalate	$\frac{1}{2}(C_2, O_4)^{--}$	99,800

CHAPTER III.

THE USE OF THE THERMOCHEMICAL DATA.

Simple Combinations.

If the problem is the simple calculation of how much heat is evolved in the combination of a given weight of one element with another, the factors needed, the heat evolved per unit weight of substance combining, are obtained by a simple division from the thermochemical data given. Thus, suppose the question to be the total heat evolved in Problem 3, in the oxidation in a Bessemer converter of

100 kilos. of carbon to carbonic oxide.
200 kilos. of carbon to carbonous oxide.
50 kilos. of manganese to MnO.
150 kilos. of silicon to SiO^2.
500 kilos. of iron to FeO.

The solution would be

$$100\times\frac{97,200}{12} = 100\times8100 = 810,000 \text{ Calories.}$$

$$200\times\frac{29,160}{12} = 200\times2430 = 486,000 \text{ "}$$

$$50\times\frac{90,900}{55} = 50\times1653 = 82,650 \text{ "}$$

$$150\times\frac{180,000}{28} = 150\times7000 = 1,050,000 \text{ "}$$

$$500\times\frac{65,700}{56} = 500\times1173 = 586,500 \text{ "}$$

$$\text{Total } 3,015,150 \text{ "}$$

Complex Combinations.

If the problem is a step more complex, that is, includes the combination of compounds with each other to form a more

complex compound, the molecular weights are still our guide, together with the thermochemical data given. If, for instance, the question above solved is complicated by the further requirement, to add the heat evolved by the formation of the slag, that is, of the MnO and FeO with SiO^2 to form silicate, we may calculate the heat of union of FeO and MnO with SiO^2 as follows:

$(Mn, Si, O^3) = 276{,}300$ Calories.
But $(Mn, O) = 90{,}900$ "
and $(Si, O^2) = 180{,}000$ "
therefore $(MnO, SiO^2) = 5{,}400$ "

$$\text{or, per kilo. of MnO} = \frac{5{,}400}{71} = 76 \text{ Calories.}$$

Similarly

$(Fe, Si, O^3) = 254{,}600$ Calories.
$(Fe, O) = 65{,}700$ "
$(Si, O^2) = 180{,}000$ "
$(FeO, SiO^2) = 8{,}900$ "

$$\text{per kilo. of FeO} = \frac{8{,}900}{72} = 124 \text{ Calories.}$$

Therefore the additional heat of formation of the slag may be

Wt. MnO = 64.5 kilos. × 76 = 4,902 Calories.
Wt. FeO = 642.8 " ×124 = 79,707 "
Sum = 84,609 "

Similar principles of calculation apply to all the oxygen-containing salts. Thus, if from the heat of formation of any sulphate we subtract the heat of formation of SO^3, and also of the metallic oxide present, the residue is the heat of combination of the metallic oxide with SO^3,—the weights involved being always those represented by the formulæ. Thus, calling MO any metallic oxide, we may express the principle as follows:

$(MO, SiO^2) = (M, Si, O^3) - (M, O) - (Si, O^2)$
$(MO, SO^3) = (M, S, O^3) - (M, O) - (S, O^3)$
$(MO, CO^2) = (M, C, O^3) - (M, O) - (C, O^2)$
$(3MO, P^2O^5) = (M^3, P^2, O^8) - 3(M, O) - (P^2, O^5)$
etc. etc.

Example.—What is the heat required to calcine limestone?

$$(CaO, CO^2) = (Ca, C, O^3) - (Ca, O) - (C, O^2)$$
$$= 273{,}850 - 131{,}500 - 97{,}200$$
$$= 45{,}150 \text{ Calories.}$$

This is the heat required to split up $CaCO^3$ (100 parts) into CaO (56) and CO^2 (44); the heat required is therefore

$45{,}150 \div 100 = 451.5$ Calories per kilo. of $CaCO^3$ decomposed.
$45{,}150 \div 44 = 1026.$ " " " CO^2 driven off.
$45{,}150 \div 56 = 806.$ " " " CaO remaining.

And either of these quantities may be used, according to convenience in working the problem.

Double Decompositions.

If the thermochemical problem involves the simultaneous decomposition of one or more substances and formation of one or more others, then the chemical equation should be written, and a thermochemical interpretation given of all the energy involved in the passage from starting compounds to products. Every chemical equation can be thus interpreted, if the heats of formation of all the compounds represented in it are known. We obtain the net energy of the reaction by assuming that all the substances used are resolved into their elements, and that all the products are formed from their elements; the first item is therefore to add together the heats of formation of all the substances used, starting with their elements, and by changing the algebraic sign of this sum we have the heat necessary to decompose the substances used into their elements; the second item is similarly found by adding together the heats of formation of all the substances formed; the difference between these two items is the net energy of the reaction. In making these summations, regard must, of course, be paid to the number of molecules of each substance concerned, as shown in the reaction (because the tabulated data are the heats of formation of one molecule only) and to the algebraic sign of the heats of formation.

Examples.—(a) What heat is evolved when dry ferric oxide is reduced by aluminium, in the Goldschmidt "Thermite" process?

$$\begin{array}{l|l} Fe^2O^3+2Al = & Al^2O^3+2Fe \\ -195{,}600 & +392{,}600 \\ \hline & +197{,}000 \text{ Calories.} \end{array}$$

(b) Write the equation showing the reaction of metallic sodium on water in excess:

$$\begin{array}{l|l} 2H^2O+2Na = 2NaOH+H^2+\text{aq. (excess water)} & \\ -2(69{,}000) & +2(112{,}500) \\ \hline -138{,}000 & +225{,}000 \\ \hline & +87{,}000 \text{ Calories.} \end{array}$$

(c) What heat is evolved in the reaction of water on calcium carbide to form acetylene gas?

$$\begin{array}{l|l} CaC^2 \quad +2H^2O = CaO^2H^2+ \quad C^2H^2 & \\ -(-6250)-138{,}000 & +215{,}600+(-54{,}750) \\ \hline -131{,}750 & +160{,}850 \\ \hline & +29{,}100 \end{array}$$

The last case leaves out the very small heat of solution of the calcium hydrate which would normally go into solution. If such a large excess of water was used that all the calcium hydrate formed could dissolve, the heat of formation of the hydrate in dilute solution, 219,500 Calories, would be used, and the final result would be 33,000 Calories. The case is also very instructive, because it contains two compounds which are endothermic, that is, their heat of formation is negative, and therefore, as in the case of CaC^2, heat is given out when it decomposes, while in the case of C^2H^2 heat is absorbed when it is formed.

(d) What are the heats of combustion of the gaseous hydrocarbons which form constitutents of common fuels, expressed per cubic meter of gas burning, and with the water formed assumed remaining as vapor, uncondensed? To calculate these we write the equations of combustion, with water as gas, and find the sum total of heat evolved; since every molecule of gas burning represents 22.22 m^3 of gas, we can, by a simple division, obtain the value sought.

Methane:

$$CH^4 + 2O^2 = CO^2 + 2H^2O$$
$$-22{,}250 \mid +97{,}200 + 2(58{,}060)$$
$$+191{,}070 \text{ Calories.} = 8{,}598 \text{ per m}^3 \text{ CH}^4.$$

Ethane:

$$2C^2H^6 + 7O^2 = 4CO^2 + 6H^2O$$
$$-2(26{,}650) \mid +4(97{,}200) + 6(58{,}060)$$
$$+683{,}860 \text{ Calories.} = 15{,}387 \text{ per m}^3 \text{ C}^2\text{H}^6.$$

Propane:

$$C^3H^8 + 5O^2 = 3CO^2 + 4H^2O$$
$$-33{,}850 \mid +3(97{,}200) + 4(58{,}060)$$
$$+489{,}990 \text{ Calories.} = 22{,}050 \text{ per m}^3 \text{ C}^3\text{H}^8.$$

By applying these principles to all the hydrocarbons whose heat of formation has been given in the tables, we obtain the following useful table, water being considered as uncondensed and cold:

Hydrocarbon.	*Molecular Heat of Combustion.* Calories.	*Heat of Combustion of* 1 m³ (Calories)	1 ft³ (B.T.U.)
Methane (gas)	191,070	8,598	966
Ethane (gas)	341,930	15,387	1728
Propane (gas)	489,990	22,050	2477
Ethylene (gas)	321,770	14,480	1627
Propylene (gas)	471,830	21,232	2385
Toluene (liquid)	906,990	.....	....
Benzene liquid	758,130	.....	....
Benzene gas	765,330	34,440	3869
Turpentine liquid	1,428,930	.....	....
Turpentine gas	1,438,330	64,725	7271
Naphthaline solid	1,223,690	.....	....
Naphthaline liquid	1,228,290	55,273	6209
Anthracine (solid)	1,690,150	.....	....
Acetylene (gas)	307,210	13,825	1555
Methyl alcohol liquid	148,270	.....	....
Methyl alcohol gas	156,670	7,050	799
Ethyl alcohol liquid	295,330	.....	....
Ethyl alcohol gas	305,430	13,744	1544

		Molecular Heat of Combustion.	*Heat of Combustion of*	
Acetone	liquid.....	396,130	.....	....
	gas.....	403,630	18,163	2040

(To the above we will add data for three other common gaseous fuels.)

Carbonous oxide (gas)	68,040	3,062	344
Hydrogen (gas).....	58,060	2,613	293.5
Hydrogen sulphide.....	122,520	5,513	619

Calorific Power of Fuels.

By using the principles explained we can calculate the calorific power of any combustible, with the aid of one or two simple assumptions. Regarding the water formed, we will consider in all ordinary metallurgical calculations that it remains uncondensed, thus putting it on the same footing as the other products of combustion. This amounts virtually to assuming that the latent heat of condensation of the vapor formed has not been generated in the furnace, an assumption which is quite justified if, as is almost always the case, the water formed inevitably escapes as vapor. If, in any special case, the products of combustion are in reality cooled down so far that the water does condense, then it would be proper to assume the higher calorific powers for the combustion of the hydrogen-containing materials, and thus a more accurate heat-balance of the furnace operation could be constructed. An instance of the latter might be the case of the partial combustion of a fuel in a gas producer, where the fuel gas is afterwards cooled before using, in order to condense from it ammonia water, etc. (Mond's producer). In this case, it is possible that some water formed by the partial combustion would be afterwards condensed, and to obtain a correct heat-balance-sheet of the producer it would be necessary to assume that this heat had also been generated. Such cases occur very rarely in metallurgical practice, and it is therefore recommended to always use the lower calorific values, assuming water vapor uncondensed and its latent heat of condensation not to have been generated—unless the conditions of the problem point plainly to the opposite course as correct. It is no more correct to charge against a furnace the latent heat of condensation of the

water vapor formed, than it would be to charge against it the latent heat of condensation of the carbonic oxide formed, if the conditions of practice are such that it is impossible to utilize in any useful manner either one of them. Those who persist in assuming that the latent heat of vaporization of the water formed by combustion is generated in and chargeable against the furnace, and then, of necessity, charge the same quantity against the heat carried off in the products of combustion, are in the great majority of cases adding to both sides of the balance sheet a quantity which cannot possibly be utilized, and are therefore distorting all the factors of heat generation and distribution. By thus abnormally increasing the sensible heat in the waste gases, they abnormally *decrease* the proportionate value of other items of heat distribution and utilization. I have dwelt on this matter at length, because it is of importance in furnaces using fuel, such as gas, rich in hydrogen; where, in some cases, the counting of the latent heat of condensation of the water vapor formed in the escaping gases, would perhaps *double* the apparent chimney loss, and give distorted values to the whole heat balance sheet. What we are after, in every case, are the real facts and figures as to the working of a furnace or operation, and we must therefore judge the operation by a theoretically perfect standard, it is true, but not by a theoretically impossible standard; *i.e.*, our standard must be the theoretically possible one under the practical conditions necessarily prevailing. A radical reform is very much needed in just this respect,—in the treatment of the latent heat of vaporization of the water formed—by writers on metallurgical processes and problems of combustion.

Problem 4.

A natural gas from Kokomo, Ind., contained by analysis: CH^4 94.16, H^2 1.42, C^2H^4 0.30, CO^2 0.27, CO 0.55, O^2 0.32, N^2 2.80, H^2S 0.18 per cent.

Required:

(1) What is its metallurgical calorific power per cubic meter and per cubic foot?

(2) Comparing it with coal, having a calorific power of 8,000 Calories, how much gas gives the same generation of heat as a metric ton of coal?

(3) If the natural gas costs $0.15 per 1,000 cubic feet, at what price per metric ton would the coal furnish heating power at the same cost for fuel?

Solution.—Requirement (1) Heat of combustion of 1 cubic meter:

CH^4 0.9416 ×	8,598 =	8095.9	Calories.
H^2 0.0142 ×	2,613 =	37.1	"
C^2H^4 0.0030 ×	14,480 =	43.4	"
CO 0.0055 ×	3,062 =	16.8	"
H^2S 0.0018 ×	5,513 =	9.9	"
	Total =	8203.1	"

In British thermal units per cubic foot we have

$$8{,}203.1 \times 3.967 \div 35.314 =$$
$$8{,}203.1 \times 0.11233 = 921.5 \text{ B. T. U. per ft}^3 \text{ (1)}$$

Requirement (2):

$$\frac{8000 \times 1000}{8{,}203.1} = 975 \text{ m}^3$$
$$= 34{,}450 \text{ ft}^3.$$

If the ton of coal be taken as 2240 pounds, instead of the metric ton of 2204 pounds, the equivalent volume is

$$34{,}450 \times \frac{2240}{2204} = 35{,}013 \text{ ft}^3.$$

Requirement (3):

$$\frac{34{,}450}{1000} \times 0.15 = \$5.16\tfrac{3}{4} \text{ per metric ton.}$$

or, per ton of 2240 pounds,

$$\$5.16\tfrac{3}{4} \times \frac{2240}{2204} = \$5.25 \text{ per long ton.}$$

DULONG'S FORMULA.

When a solid or liquid carbonaceous fuel is to be burned, its calorific power may either be determined directly in a calorimeter (which is the best way, if carefully done), or may be calculated from its analysis. In case it is determined calori-

metrically, the weight of water produced per unit of fuel should be determined either in the same or by a separate experiment, and the latent heat of vaporization of this water subtracted from the calorimetric value of the fuel, in order to get its metallurgical, or practical, calorific power.

Example.—A coal gave 9215 calories per gram in the calorimeter, and its products of combustion gave up 0.45 grams of condensed water. What is its practical calorific power?

Taking the products cold, the heat of condensation per gram of water vapor may be taken as 606.5 calories (Regnault), and we therefore have obtained in the calorimeter

$$0.45 \times 606.5 = 273 \text{ Calories}$$

more than if the products were cold and water uncondensed. The practical calorific power is therefore

$$9215 - 273 = 8942 \text{ Calories per kilogram.}$$

Dulong's simple formula, or method of calculation, is the statement that the calorific power of a fuel can be calculated from the amount of carbon, hydrogen, and oxygen it contains by assuming all the carbon free to burn, the oxygen to be all combined with hydrogen in the proportions of O^2 to $2H^2$ (32 to 4), and that the rest of the hydrogen is free to burn.

Example.—Taking the bituminous coal of Problem 1, containing carbon 73.60, hydrogen 5.30, nitrogen 1.70, sulphur 0.75, oxygen 10.00, moisture 0.60, ash 8.05, its calculated calorific power is per kilogram:

Carbon	$0.7360 \times$	8100 =	5962 Calories.	
Hydrogen	0.0530			
	0.0125			
	$0.0405 \times$	34,500 =	1397 "	(water liquid)
Sulphur	$0.0075 \times$	2164 =	17 "	
		Total	7376 "	

This calculation is made, however, on the assumption that all the water in the products is condensed to liquid, *i.e.*, not only the water formed by combustion of the free hydrogen, but also the already-formed H^2O containing the oxygen of the coal, as well as the moisture present to start with. To obtain

the practical calorific power by calculation we must subtract from the above-generated heat the latent heat of *all* the vapor of water in the products, as follows:

Moisture in coal	0.0060 kilos.
Moisture formed by combined hydrogen	0.1125 "
Moisture formed by free hydrogen	0.3645 "
Total	0.4830 "

Latent heat of vaporization = $606.5 \times 0.4830 = 293$ Calories.
Practical calorific power, water all as vapor = 7083 Calories.
The values thus calculated are found to agree satisfactorily with the laboratory and the practical calorific powers of the fuels.

The Theoretical Temperature of Combustion.

If we start with a cold fuel and cold air the maximum temperature which can be obtained by the combustion is simply that temperature to which the heat generated can raise the products of combustion, assuming that all that heat resides primarily in the products as sensible heat. This is then a problem in physics, in which we have a known amount of heat available, and the question is to what temperature it will raise the products of combustion. The problem is at once soluble when we know the mean specific heats of the products of combustion and their respective quantities.

Until a few years ago these specific heats at high temperatures were unknown, and very false results were obtained by assuming constant specific heats from ordinary temperatures up, and values were thus calculated which were known to be hundreds, and in some cases, thousands, of degrees too high. The most satisfactory values for the specific heats of the fixed gases and water vapor and carbonic oxide are those determined by Mallard and Le Chatelier, and their proper use has entirely solved the question of theoretical temperatures of combustion, and removed a positively disgraceful discrepancy between theory and practice. The specific heats of these gases increase with temperature, so that the actual specific heat of a cubic meter (measured at standard conditions) is, at the temperature t,—

for N^2, O^2, H^2, CO —S = 0.303 + 0.000054t
" " CO^2—S = 0.37 + 0.00044t
" " (vapor) H^2O—S = 0.34 + 0.00030t

For calculating the quantity of heat needed to raise the gas from O° to t°, however, we need the mean specific heats, Sm, between O° and t°. These are, of course, the above constants plus half the increase, viz.:

for N^2, O^2, H^2, CO—Sm = 0.303 + 0.000027t
" CO^2—Sm = 0.37 + 0.00022t
" (vapor) H^2O—Sm = 0.34 + 0.00015t

and the quantity of heat needed to raise 1 cubic meter (at standard conditions) from O° to t° is

for N^2 O^2 H^2, CO—Q (o-t) = $0.303t + 0.000027t^2$
" CO^2—Q (o-t) = $0.37t + 0.00022t^2$
" H^2O—Q (o-t) = $0.34t + 0.00015t^2$

or, finally, the quantity of heat needed to raise 1 cubic meter (measured at standard conditions) from t to t′ is

for N^2, O^2, H^2, CO—Q (t′-t) =
$0.303\ (t'-t) + 0.000027\ (t'^2-t^2)$
" CO^2—Q (t′-t) =
$0.37\ (t'-t) + 0.00022\ (t'^2-t^2)$
" H^2O—Q (t′-t) =
$0.34\ (t'-t) + 0.00015\ (t'^2-t^2)$

And the mean specific heat, Sm, between any two temperatures is

for N^2 O^2, H^2, CO —Sm (t′-t) =
$0.303 + 0.000027\ (t'+t)$
" CO^2 —Sm (t′-t) =
$0.37 + 0.00022\ (t'+t)$
" H^2O —Sm (t′-t) =
$0.34 + 0.00015\ (t'+t)$

Examples:

(1) What is the temperature of the hottest part of the oxy-hydrogen blowpipe flame?

According to the equation $2H^2 + O^2 = 2H^2O$, the hydrogen gas forms an equal volume of water vapor. (Equal numbers of molecules.) The heat of combustion of one cubic meter of hydrogen is 2613 Calories. The question is, therefore: " To

what temperature will 2613 Calories raise one cubic meter of water vapor?" The answer is, using the data above,

$$Q\ (o\text{-}t) = 0.34t + 0.00015t^2 = 2613$$

Whence $t = 3191°$

(2) What is the maximum temperature of the hydrogen flame burning in dry air?

The heat evolved is, as before, 2613 Calories, and there is formed also one cubic meter of water vapor, but the products will contain also the nitrogen which accompanied the 0.5 cubic meter of oxygen necessary for combustion, viz.: $\frac{0.5}{0.208} - 0.5$ = 1.9 cubic meters, and this is heated as well as the water vapor. Therefore,

$$Q\ (o\text{-}t) = (0.34t + 0.00015t^2) + 1.9\ (0.303t + 0.000027t^2) = 2613$$

Whence $0.916t + 0.0002013t^2 = 2613$

And $t = 2010°$

(3) What is the temperature of the air-hydrogen blowpipe, if 25 per cent. excess of air is used, above that required?

All the data are the same as above, except that to the products will be added $0.25\ (0.5 + 1.9) = 0.6$ cubic meters of unused air, which has the same specific heat as nitrogen, and therefore the equation becomes

$$Q\ (o\text{-}t) = (0.34t + 0.00015t^2) + 2.5\ (0.303t + 0.000027t^2) = 2613$$

Whence $t = 1764°$

This calculation brings out very clearly the uselessness and ineffectiveness of using more air than is theoretically necessary; any excess simply passes unused into the products of combustion, and thus reduces their maximum possible temperature. The obtaining of the maximum possible temperature depends upon accurately proportioning the supply of oxygen or air to the quantity of gas burned; an excess or a deficiency will result in a lower temperature.

Combustion with Heated Fuel or Air.

If the fuel itself or the air which burns it is preheated, the sensible heat in either one or in both is simply added to the heat generated by the combustion, to give the total amount of

heat which must be present as sensible heat in the products of combustion. The effect is exactly the same as if the heat developed by combustion had been increased by the sensible heat in the fuel or air used.

What is the calorific intensity (theoretical maximum temperature) obtained by burning carbonous oxide gas? (a) Cold, with cold air; (b) cold, with hot air at 700° C.; (c) hot, with hot air, both at 700° C.

(a) Take one cubic meter of carbonous oxide. Calorific power 3,062 Calories; product one cubic meter of carbonic oxide, and 1.904 cubic meters of nitrogen.

Let t be the temperature attained; then

Heat in the 1 m^3 carbonic oxide $= 0.37t + 0.00022t^2$
" " 1.904 m^3 nitrogen gas $= 0.577t + 0.0000514t^2$
" " products = 3,062 Cal's. $= 0.947t + 0.0002714t^2$
Whence $t = 2050°$

(b) If the 2.404 cubic meters of air needed are preheated to 700° C., they will bring in as sensible heat

$$Q\ (o\text{-}700) = 2.404\ [0.303\ (700) + 0.000027\ (700)^2$$
$$= 552 \text{ Calories.}$$

The total heat in the products will be $3062 + 552 = 3614$ Calories, and therefore $0.947t + 0.0002714t^2 = 3614$
Whence $t = 2189°$

(c) If the gas itself is also preheated it brings in

$$Q\ (o\text{-}700) = 0.303\ (700) + 0.000027\ (700)^2$$
$$= 225 \text{ Calories.}$$

The total heat in the products will be $3614 + 225 = 3839$ Calories, and therefore $0.947t + 0.0002714t^2 = 3839$
Whence $t = 2284°$

Heating both gas and air to 700° before they burn thus raises the theoretical temperature from 2050 to 2284 or 234°.

Problem 5.

Statement.—The natural gas of Kokomo, Ind., contains by analysis: Methane (marsh gas) 94.16, ethylene (olefiant gas)

0.30, hydrogen 1.42, carbonous oxide 0.55, carbonic oxide 0.27, oxygen 0.32, nitrogen 2.80, hydrogen sulphide 0.18,—in percentages, by volume.

Required:

(1) The maximum flame temperature, if burned cold with the theoretical amount of cold, dry air necessary.

(2) The calorific intensity, if burned cold, with the requisite air preheated to 1000° C.

(3) The calorific intensity, if burned cold, with 25 per cent. more air than theoretically necessary, preheated to 1000°.

Solution:

[The practical calorific power of this gas has been already calculated in Problem 4 as 8203 Calories per cubic meter. The gas itself is always burned cold, because, if preheated, it decomposes and deposits carbon in the regenerators.]

The products of combustion of the gas, say per cubic meter, must first be found, using the formulæ for combustion.

Requirement (1):

	1 Cubic Meter of Gas.	Oxygen Needed. m^3	Products. CO^2	H^2O	SO^2	N^2
CH^4	0.9416	1.8832	0.9416	1.8832	....	....
C^2H^4	0.0030	0.0090	0.0060	0.0060	....	....
H^2	0.0142	0.0071	....	0.0142	....	....
CO	0.0055	0.00275	0.0055	....	....	....
CO^2	0.0027	....	0.0027	....	....	....
O^2	0.0032	0.0032	....	....	....	....
N^2	0.0280	....	....	....	....	0.0280
H^2S	0.0018	0.0027	....	0.0018	0.0018	....
		1.90155	0.9558	1.9052	0.0018	0.0280
Air required		9.14		(carrying in N^2) =		7.238
					Total N^2	7.266

The heat generated will exist as sensible heat in the CO^2, H^2O, SO^2 and N^2 of the products. The mean specific heat of SO^2 per cubic meter is 0.444 at ordinary temperatures; what it is at high temperature has not been determined; we will give it the same index of increase as the analogous gas CO^2,

and take for it Sm (o-t) = 0.444+0.00027t, or Q (o-t) = 0.444t+0.00027t².

At the temperature attained by combustion, t, the products will contain the following amounts of heat:

$$N^2 = 7.266 \quad (0.303t + 0.000027t^2)$$
$$H^2O = 1.9052 \quad (0.34t + 0.00015t^2)$$
$$CO^2 = 0.9558 \quad (0.37t + 0.00027t^2)*$$
$$SO^2 = 0.0018 \quad (0.444t + 0.00027t^2)$$
$$\text{Total} = 3.2044t + 0.00074057t^2 = 8203 \text{ Calories.}$$

From which $t = 1806°$ (1)

Requirement (2):

Heat in 1 m³ of air at 1000° = 0.303 (1000) + 0.000027 (1000)².
= 330 Calories.
" 9.14 m³ " 1000° = 3016 "
Therefore: $3.2044t + 0.00074057t^2 = 8203 + 3016$
Whence $t = 2288°$

Requirement (3):

Excess air used = 9.14×0.25. = 2.285 m³.
Heat in 11.425 m³ at 1000° = 11.425×330 = 3770 Calories.

The heat capacity of the excess air must be added to the heat in the products at temperature t, viz.:

$$\text{Excess air} = 2.285 \ (0.303t + 0.000027t^2)$$

making the total heat in the products (adding to previous expression):

$$3.8968t + 0.00080227t^2 = 8203 + 3770$$
Whence $t = 2134°$

The Eldred Process of Combustion.

A means of regulating the temperature of the flame has been proposed by Eldred, and described by Mr. Carlton Ellis in the December, 1904, issue of *El. Chem. Ind.* The proposition is simply to mix with the air used for combustion a certain

* These and some succeeding problems were worked out using this specific heat. Later the author has adopted a slightly different value for CO^2, viz., (0.37+0.00022t), which he now considers more nearly correct.

proportion of the products of combustion themselves. The principle is easily understood when the requisite calculations of the theoretical flame temperatures are made. When solid fuel is burnt the temperature is often too high locally, and results in burning out grate bars or overheating the brick work of the fire-place, or overheating locally the material which is mixed with the fuel. If the air is diluted with products of combustion the initial theoretical temperature is lowered, and the above evils may be obviated. Using solid fuel, the heat in the fuel before the air actually burns it must be added to the heat generated by combustion to get the actual temperature in the hottest part of the fire.

Examples: (1) What will be the highest temperature in a charcoal fire fed by air, assuming complete combustion without excess of air?

Assuming the charcoal to be pure carbon, and to be heated to the maximum temperature t before it burns (by the combustion of the preceding part), the heat available is:

Heat of combustion of 1 kilo of carbon.....		8100 Cal's.
Sensible heat in the carbon at t°.....	0.5t—120	"
Total heat available to raise the temperature...	7980 + 0.5t	"
Products of combustion....	CO^2 1.85 m^3	
	N^2 7.04 "	
Heat of product at t°.....	CO^2 1.85 $(0.37t + 0.00022t^2)$	
	N^2 7.04 $(0.303t + 0.000027t^2)$	
	Sum $2.81t + 0.00060t^2$	

therefore $2.81t + 0.00060t^2 = 7980 + 0.5t$

whence $t = 2199°$

(2) What will be the temperature in the same case, if the air used is diluted with an equal volume of the products of combustion?

The heat available is the same as before, $7980 + 0.5t$; but since the mixed air for combustion contains only half as much oxygen per cubic meter, the products will be exactly doubled in amount for a unit weight of carbon burnt, and we therefore have directly

$$2\,(2.810t + 0.00060t^2) = 7980 + 0.5t$$

whence $t = 1213°$

It is therefore evident that the maximum temperature of the hot gases at their moment of formation is nearly halved by the procedure stated.

(3) Taking the cases cited by Mr. Ellis, where the products contained originally 15 per cent. oxygen and 6 per cent. carbon dioxide, and after mixing the air used with half its volume of the chimney gases, 9 per cent. oxygen and 12 per cent. carbon dioxide (the gas-air mixture entering containing 15 per cent. oxygen and 6 per cent. carbon dioxide), what are the maximum temperatures obtained in the two cases?

Case 1: The heat available is as before; the products of combustion are CO^2 1.85 m^3, O^2 4.62 m^3, N^2 24.36 m^3, and their sensible heat at temperature t—

$$\begin{aligned} \text{Heat in } CO^2 &= 1.85\ (0.37t + 0.00027t^2) \\ \text{“ } \quad O^2+N^2 &= 28.98\ (0.303t + 0.000027t^2) \\ \text{Sum} &= 9.46t + 0.00128t^2 \end{aligned}$$

therefore $9.46t + 0.001280t^2 = 7980 + 0.5t$
whence $t = 800°$

Case 2: The products, per kilogram of carbon burnt, will be CO^2 3.70 m^3, O^2 2.77 m^3, N^2 24.36 m^3, and we have

$$\begin{aligned} \text{Heat in } CO^2 &= 3.70\ (0.37t + 0.00027t^2) \\ \text{“ } \quad O^2+N^2 &= 27.13\ (0.303t + 0.000027t^2) \\ \text{Sum} &= 9.09t + 0.00173t^2 \end{aligned}$$

therefore $9.09t + 0.00173t^2 = 7980 + 0.5t$
whence $t = 764°$

Conclusions: The calculations regarding the Eldred process bring out what was not stated in the printed description of the method, viz.: that if a small excess, or no excess of oxygen escapes, to the chimney, the temperature of the flame will be greatly reduced by the dilution of the air used, because more gas-air mixture will be required per unit of fuel burnt; but if there is any large amount of unused oxygen escaping in the first instance, the dilution practiced will scarcely affect the temperature of the flame at all, because it makes very little difference whether the fuel is heating up unused oxygen or carbon dioxide dilutant substituted for some of it, as long

as there is more than enough oxygen to burn the fuel. The fact of the specific heat of carbon dioxide being greater than that of oxygen, is the only reason for the small calculated difference of 36°, in cases 1 and 2. It is true that the dilution practiced will result in less heat being lost in the waste gases, in the *Example* (3), but the same economy could be obtained by simply using less excess of air in the first instance.

Temperatures in the "Thermit" Process.

The Goldschmidt porcess of reducing metallic oxides by powdered aluminium, igniting the cold mixture, is only a special case of our general rule, as far as concerns the calculation of the theoretical temperatures obtained. In any case, the total heat available is the surplus evolved in the chemical reaction, and the temperature sought is that to which this quantity of heat will raise the products of the reduction. The products are alumina and the reduced metal. The heat in the latter, in the melted state, is well known in many cases; it is most clearly expressed by the sum of the heat in such melted metal just at its melting point (which is easily determined calorimetrically, and is well known for many metals), plus the heat in the melted metal from the melting point to its final temperature, which is equal to t, minus the melting temperature, multiplied by the specific heat in the melted condition These data are known for many metals; for some they may have to be assumed from some general laws correlating these values. The heat in melted alumina has not been determined calorimetrically, to my knowledge. Its sensible heat solid is $0.2081t + 0.0000876t^2$ (determination made in author's laboratory), which, evaluated for the probable melting point, 2200° C., would give the heat in it at that temperature 881.8 Calories; the latent heat of fusion of molecular weight is very probably 2.1 T, where T is the absolute temperature of the melting point, making the latent heat of fusion per kilogram $2.1 (2200 + 273) \div 102 = 5193 \div 102 = 50.9$ Calories. The specific heat in the melted state is probably equal to the specific heat of the solid at the melting point, viz.: $0.2081 + 0.0001752 (2200) = 0.5935$. We, therefore, have for the heat in melted alumina at temperature t—

Heat in solid alumina to the melting point..... 881.8 Calories
Latent heat of fusion..... 50.9 "
Heat in liquid alumina to its setting point 0.5935 (t-2200)

Total.932.7+0.5935 (t-2200)

or, for a molecular weight, 102 kilograms: 95,135+60.54 (t-2200).

Examples:

(1) If black cupric oxide is reduced by powdered aluminium what is the temperature attained?

The reaction is

$$3CuO + 2Al = Al^2O^3 + 3Cu$$
$$-3\ (37{,}700) \quad | + 392{,}600$$
$$+279{,}500$$

The products must therefore be raised to such a temperature that they contain 279,500 Calories. The heat in molecular weight of alumina at temperature t has already been found; that in copper at t° is, for one kilogram (using the author's determinations):

Heat in melted copper at setting point = 162 Calories.

Heat in melted copper above 1065° = 0.1318 (t—1065) Calories.

Total = 162+0.1318 (t—1065).

Per atomic weight (63.6 kilos.) = 10303+8.3825 (1—1065)

From these data there follows the equation:

$$95{,}135 + 60.54\ (t-2200) + 3[10{,}303 + 8.3825\ (t-1065)] = 279{,}500$$

whence $t = 3670°$

A little further calculating will show that approximately one-third of all the heat generated exists in the copper, and two-thirds in the melted alumina.

(2) If pure ferric oxide is reduced by the " Thermit " process, what is the temperature of the resulting iron and melted alumina?

The reaction and the heat evolved have been already given in the preceding discussion of these calculations (page 44.) They show that per molecular weight of alumina formed there are two atomic weights (112 kilos.) of iron formed, and there is disposable altogether 197,000 Calories. The heat in a kilo-

gram of pure iron at its melting point (1600°) is 300 Calories, the latent heat of fusion approximately 69 Calories, and the specific heat in the melted condition 0.25. The total heat in a kilogram of melted iron is therefore $369+0.25$ (t—1600) Calories, or per atomic weight = $20,664+14$ (t—1600) Calories.

We, therefore, can write the equation:

$$95,135+60.54\ (t—2200)+2[20,664+14\ (t—1600)] = 197,000$$

whence $t = 2694°$

A similar calculation made for the reduction of MnO by the theoretical amount of aluminium, shows a reduction temperature less than the melting point of alumina. This would mean that the melting down of the mass to a fused slag of pure alumina could not take place. What happens in the reduction of manganese is that an excess of manganous oxide is used, whereby all the aluminium is consumed, and none at all gets into the reduced manganese, and, furthermore, the excess of manganous oxide unites with the alumina to form a slag of manganous aluminate, which is fusible at the temperature attained. Without the latter arrangement no fused slag could result.

Similar calculations, made with silicon as the reducing agent, show similar difficulties regarding the theoretical temperatures attainable, when iron or manganese are reduced. By using an excess of the oxides of these metals, however, calculation shows that temperatures sufficient to fuse the metals and the manganous silicate, or ferrous silicate produced, ought to be obtained.

CHAPTER IV.

THE THERMOCHEMISTRY OF HIGH TEMPERATURES.

The problem is: Knowing the heat evolved (or absorbed) in the formation of a compound, or in a double reaction, starting with the reacting materials cold, and ending with the products cold, what is the heat evolved (or absorbed) in either of the following cases?

(*a*) Starting with the reagents cold and ending with the products hot.

(*b*) Starting with the reagents hot and ending with the products hot.

(*c*) Starting with the reagents hot and ending with the products cold.

Of these three cases (*b*) is the most general form of the problem, and occurs frequently in metallurgical practice, particularly in electrometallurgy; (*a*) is a more limited form, and requires less data for its calculation, while it is very frequently the desideratum in discussing the thermochemistry or heat requirements of a metallurgical process; (*c*) is derivable at once if the data exist for calculating (*b*), and is of such rare occurrence in practice that we can dispense with its lengthy discussion.

The thermochemical data already given and described in preceding sections enable us to calculate the heat of any chemical reaction starting with cold reagents and ending with the products cold. For instance: (Zn, O) = 84,800 Calories means that if we take 65 kilograms of solid zinc, at room temperature, and 16 kilograms of oxygen, as gas at room temperature, ignite them, and after the reaction cool the 81 kilograms of zinc oxide formed down to the same starting temperature, there will be developed a total of 84,800 Calories. Similarly, using the datum (C, O) = 29,160 Calories, we can construct

gram of pure iron at its melting point (1600°) is 300 Calories, the latent heat of fusion approximately 69 Calories, and the specific heat in the melted condition 0.25. The total heat in a kilogram of melted iron is therefore $369+0.25\ (t—1600)$ Calories, or per atomic weight $= 20{,}664+14\ (t—1600)$ Calories.

We, therefore, can write the equation:

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whence $t = 2694°$

A similar calculation made for the reduction of MnO by the theoretical amount of aluminium, shows a reduction temperature less than the melting point of alumina. This would mean that the melting down of the mass to a fused slag of pure alumina could not take place. What happens in the reduction of manganese is that an excess of manganous oxide is used, whereby all the aluminium is consumed, and none at all gets into the reduced manganese, and, furthermore, the excess of manganous oxide unites with the alumina to form a slag of manganous aluminate, which is fusible at the temperature attained. Without the latter arrangement no fused slag could result.

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and interpret the reduction reaction, starting with cold materials and finally ending with cold materials, as follows:

$$\begin{array}{c|c} ZnO + C = Zn + CO \\ -84{,}800 \quad | \quad +29{,}160 \\ \hline -55{,}640 \end{array}$$

This reaction, as interpreted, stands for none of the above cases (*a*), (*b*) or (*c*); in fact, it represents only a calorimetric determination in the laboratory, and does not correspond to either of the three cases actually taking place in practice, that is, it is not directly applicable to practical conditions, without being modified by the conditions actually arising in practice.

Case (*a*): If we, in practice, start with the reagents cold, and the products pass away from the furnace hot, at some determined temperature t, the total heat energy necessary to cause this transformation is calculable in two ways. The first way is to follow the course of the reaction, and to say that the total heat absorbed is that necessary to heat the reacting bodies to the temperature t, plus the heat of the chemical reaction assumed as starting and finishing at that temperature. The first of these items can be obtained if we know the sensible heat in the reacting bodies up to the temperature t; it is a question of specific heats of the reacting bodies up to t (including any physical changes of state occurring in them between o and t); the second item requires a knowledge of the heat of formation of all the compounds involved, starting with their ingredients at t, and ending with the products at t. But the latter item is the general question of the heat of a reaction starting with the ingredients hot and ending with the products hot; it is the most general case, which we have designated as *Case* (*b*), and which will be discussed later. This way of solving *Case* (*a*), therefore, really includes the solution of *Case* (*b*), and we will defer its consideration for the present. The second method of solving *Case* (*a*), and one which does not involve the more general solution, is to take the heat of the reaction, starting with the ingredients cold and ending with the products cold—the ordinary heat of the reaction from ordinary thermochemical data—and to add to this

the amount of heat which would be required to raise the products from zero to the temperature t. This, of course, does not actually represent the sequence in which the reactions take place in practice, but it accurately represents the heat involved or evolved in passing from the cold reagents to the hot products, and is, therefore, exactly the practical quantity which we are endeavoring to find. Moreover, it involves a knowledge of only the specific heats of the products, and not that of the ingredients or substances reacting.

Illustration: Starting with a mixture of zinc oxide and carbon in the proportions Zn O and C, at ordinary temperature, and shoveling them cold into a retort, how much heat is absorbed in converting them into Zn vapor and CO gas, issuing from the retort at 1300° C.?

If we start to calculate this quantity, by first finding the heat necessary to heat Zn O and C up to 1300°, that is obtained by multiplying the weights of each by their mean specific heats from 0° to 1300°, and then by 1300, as follows:

	Calories.
81 kilos. ZnO × *[0.1212 (1300) + 0.0000315 $(1300)^2$]	= 17,075
12 " C × *[0.5 (1300)—120]	= 6,360
	Sum = 23,435

To this must then be added the heat of the reaction ZnO + C = Zn + CO, starting with the reacting bodies at 1300°, and ending with the products at the same temperature. This can only be found by solving the general *Case* (*b*) for this particular reaction, which we will find involves a knowledge of the heat required to raise Zn, O, C. ZnO and CO from 0° to t. Anticipating such a solution, we may say that the heat of the reaction starting and ending at 1300° is—80,166 Calories, making the sum total of energy required 103,601 Calories.

The solution is usually much simpler if we take the second method, and add to the heat of the reaction, starting and ending at zero (—55,640 Calories), the heat required to raise 65 kilos. of zinc and 28 kilos, (22.22 cubic meters) of carbonous

* Heat in 1 kilo of carbon, for temperature above 1,000°, 0.5 t − 120 (deduction from Weber's results); zinc oxide 0.1212 t + 0.0000315 t^2 (determination by the author).

oxide, from their ordinary condition at zero to their normal condition at 1300°. The calculation for the CO gas is simply:

$$22.22\times[0.303\ (1300)+0.000027\ (1300)^2] = 9{,}766 \text{ Calories.}$$

For the zinc, the calculation is more complicated:

Heat in solid zinc to the melting point (420°):	
$65\times[0.09058\ (420)+0.000044\ (420)^2]$	= 2,977 Calories.
Latent heat of fusion 65×22.61	= 1,470 "
Heat in melted zinc, 420° to boiling point (930°):	
$65\times[0.0958+0.000088\ (420)]\times\ (930—420)$	= 4,228 "
Latent heat of vaporization (Trouton's rule) $23\times\ (930+273)$	= 27,670 "
Heat in zinc vapor (monatomic) $5\times$ (1300 —930)	= 1,850 Calories.
Sum	= 38,195 "

The total sensible heat required is, therefore, 9,766+38,195 = 47,961 Calories, which, added to the 55,640 absorbed in the chemical reaction, if it started and ended at zero, makes a total heat requirement of 103,601 Calories for the practical carrying out of this reaction, starting with the reagents cold and ending with the hot products at 1300°.

[To be absolutely accurate, regard should be paid in the above case to the fact that the above calculations are based on the substances being all at atmospheric pressure, while in the mixture of Zn vapor and CO gas each is under only 0.5 atmospheric tension. Since each of these represents a molecular weight, the outer work which has been included in the calculations is $2\times2T = 2\times2\ (1300+273) = 6292$ Calories, whereas it should really be only half that much, or 3146 Calories. The corrected heat required is, therefore, 103,601—3,146 = 100,455 Calories, or 1,545 Calories per kilogram of zinc. This datum is exactly the net heat requirement on which calculations of the net electrical energy required to produce zinc from its oxide, or calculations of the net efficiency of an ordinary zinc furnace, would be based.]

Case (b): To calculate the heat of a chemical reaction starting and finishing at any temperature t, two methods are available; The most general solution, and that easiest to understand, is to calculate for each compound involved the heat of its formation at the temperature t, that is, the heat evolved if the elements start at t and the product is cooled to t. Having these heats of formation at t, they are used in the equation in just the same manner as the heats of formation at zero are ordinarily used in obtaining the heat of the reaction starting and ending at zero. The calculations are based on this general principle: The heat evolved when the cold elements unite to form the hot product at temperature t equals the heat of union at zero, minus the heat necessary to raise the product from zero to t; if to this difference we add the heat which would be necessary to heat the uncombined elements from zero to t, the sum is the desired heat of formation at t°.

Illustration: The heat of formation of ZnO at zero is 84,800, starting with cold Zn and O and ending with cold ZnO. If we started with cold Zn and O and ended with hot ZnO, say at 1300°, the heat evolved altogether would be less than 84,800 by the sensible heat in the 81 kilograms of ZnO at 1300°, which has already been calculated (see previous illustration) to be 17,075 Calories. The difference is 67,725 Calories, and represents the transformation from cold Zn and O to hot ZnO. If the Zn and O were heated to 1300° before combining, they would contain as sensible heat the following quantities:

Heat in 65 kilograms of Zn (0 to 1300°) already calculated	38,195	Calories
Heat in 16 kilograms of O = 11.11 $m^3 \times [0.303\ (1300) + 0.000027\ (1300)^2]$ =	4,884	"
Sum	43,079	"

And the heat evolved in passing from the hot reagents to the hot product at 1300° must be 67,725 plus this sensible heat, or 110,804 Calories. We can express this datum as follows: $(Zn, O)^{1300} = 110,804$, which means that when the zinc and oxygen taken in their normal state at 1300° combine to form ZnO at 1300°, 110,804 Calories are evolved.

A similar calculation for CO is as follows:

	(C, O) =	29,160 Calories
Sensible heat in CO (0 to 1300°) already calculated =		9,766 "
Heat evolved when cold C and O form CO at 1300° =		19,394 "
Sensible heat in C (0 to 1300°) =	6360	
" " O (") =	4884	11,244 Calories
Heat evolved hot C and O to hot CO = Sum =		30,638 "
Or	$(C, O)^{1300}$ =	30,638 "

Uniting the two data found, for the heats of formation of ZnO and CO at 1300°, in the equation of reduction, we have

	ZnO + C =	Zn + CO
at 1300° =	—110,804 |	+30,638
		—80,166

The actual reduction is thus seen to absorb 24,526 Calories more at 1300° than at zero, an increase of over 42 per cent.

If to this heat of reaction at 1300° we add the heat necessary to raise the ZnO and C to 1300° (already calculated under *Case* (*a*) as 23,435 Calories), we will have a total heat requirement of 103,601 Calories, which would be required practically if we started with cold ZnO and C and ended with the hot Zn and CO. This agrees, as it indeed must, with the sum of the heat absorbed in the reaction at zero, 55,640, increased by the sensible heat in Zn and CO at 1300°, already found to be 47,961, or a total of 103,601.

Another method of calculating the heat of the reaction ZnO + C = Zn + CO at 1300°, without using the heat of formation of ZnO and CO at 1300°, is based on the following general principle: If from the heat of any reaction, starting and ending cold, there be subtracted the heat necessary to raise the products from 0 to t, the difference is the heat of the transformation from cold reagents to hot products; if to this be added the heat which would be contained in the reagents if they were heated to t, the sum is the heat of transformation from heated reagents to heated products, all at the temperature.

Illustration: The heat of the reaction we have been studying, starting and ending cold, is —55,640 Calories

Sensible heat in Zn at 1300°	= 38,195		
" " CO "	= 9,766	47,961	"
	Difference—	103,601	"
Sensible heat in ZnO at 1300°	= 17,075		
" " C "	= 6,360	23,435	"
	Sum—	80,166	"

The above is the simplest way of calculating the heat of any chemical reaction at any desired temperature, since it involves the knowledge of the heat capacities of only those substances which occur individually in the reaction, and not that of the elements of which the compounds present are composed. The above calculation, for instance, involves the heat capacities of ZnO, C, Zn, and CO, but not that of oxygen, which does not occur free in the reaction.

Case (*c*): This hardly needs discussion, because if we have the data for calculating *Case* (*b*), this case can be easily worked. If to the heat of the reaction at t° we add the heat given out by the products in cooling from t to 0, the sum is the total heat evolved in passing from the hot reagents to the cold products. This solution of the problem presupposes, however, the solution of *Case* (*b*) and requires the maximum amount of data, but it has the advantage of following and representing the logical course of the reaction. A simpler solution is to add to the heat of the cold reaction at zero, the heat necessary to heat the ingredients to t, and the sum will be the quantity required.

Illustration: Taking the same case as before:

	Heat of reaction at 1300°	= —80,166
	Sensible heat in products at 1300°	= 47,961
	Sum	= —32,205
or,	Sensible heat in reagents at 1300°	= 23,435
	Heat of reaction at zero	= —55,640
	Sum	= —32,205

The reasoning involved in the above is simply that, starting with the reagents hot and ending with the products cold, the

heat evolution must be the same whether we suppose the system to pass along the one path or the other.

General Remarks.

It will be evident from this enunciation of principles and the illustrations adduced, that for many practical purposes the calculation according to *Case* (*a*) will suffice for finding the net energy involved in many metallurgical operations; it gives the sum total of energy necessary to be supplied to pass from the cold reagents to the hot products as they come from the furnace, but the two items of which this sum is composed do not actually represent the two items of the division of this total in the furnace, *i.e.*, into heat necessary to heat the reagents to the reacting temperature and heat actually absorbed as the reaction takes place. The latter item can only be calculated by one of the two methods explained under *Case* (*b*), and then the former item can be obtained by difference, or by direct use of the heat capacities of the reacting substances.

It is, of course, obvious that this whole subject of calculating the thermochemistry of high temperatures (as distinguished from the ordinary *zero thermochemistry*) necessitates the use of all available data regarding specific heats in the solid, liquid and gaseous states of both elements and compounds, and also in many cases of their latent heats of fusion and vaporization. When, however, the necessary physical data are known, or can be assumed with approximate accuracy, the way is open to make many calculations of the greatest value in practical metallurgy and chemistry. The exact heats of formation of chemical compounds at a certain temperature, which may be, and often are, very different from these values at zero, and, having frequently different relations to each other, will explain in many cases many hitherto little understood and apparently contradictory reactions. The calculations also enable us to understand many reactions taking place only at high temperatures, to calculate whether they are really exothermic or endothermic at the temperatures at which they occur, and to compare these data with the data as to the heat of such reactions obtained by studying the chemical equilibrium of such reactions and deducing the heat of the reaction from the rate of displacement of the chemical equilibrium. One such ex-

ample may suffice to suggest the large field here open to the scientific metallurgist.

Example: G. Preuner (*Zeitschrift für Physikalische Chemie*, March 15, 1904, p. 385) reports a long and careful investigation of the equilibrium of the reaction

$$Fe^3O^4 + 4H^2 \rightleftarrows 3Fe + 4H^2O$$

in which he finds the equilibrium constant for different temperatures, and calculates from its value at 960°, by the use of Van't Hoff's formula, that the heat value of the reduction at that temperature is—11,900 Calories, and noticing the great difference between this value and the value derived from the ordinary heats of formation (—270,800 + 4(58,060) = —38,560), he concludes that the Van't Hoff formula gives wrong results when applied to this class of reactions. Now, the facts are that Preuner's observations were good, Van't Hoff's formula is correct, and applies, but the thermochemical value of the reaction,—38,560 Calories is the correct value only for *the reaction beginning and ending at ordinary temperature.* Our thermochemical principles enable us to calculate the heat of the reaction at 960°, as follows:

Heat of the reaction beginning and ending at zero = — 38,560 Calories

Heat in products at 960°:

$3Fe = 3(56) \times [0.218(960) - 39]$ Pionchon = 28,560

$4H^2O = 4(22.22) \times [0.34(960) + 0.00015.(960)^2]$ = 41,300

69,860 Calories

Heat in reagents at 960°:

$Fe^3O^4 = 232 \times [0.1447(960) + 0.0001878(960)^2]$* = 72,384

$4H^2 = 4(22.22) \times [0.303(960) + 0.000027(960)^2]$ = 28,075

100,459 "

The heat of the reaction at 960° is, therefore, according to our method of *Case* (*b*),—38,560—69,860 + 100,459 = —7,961

* Approximate determination of heat in Fe^3O^4, made recently in author's laboratory, $Q = 0.1447t + 0.0001878t^2$.

Calories. It thus appears that Preuner's dilemma was mostly caused by his thinking that the thermochemical value of the reaction at zero should be a constant for any temperature: a proper thermochemical calculation removes the dilemma.

Since the whole treatment of the subject of the thermochemistry of high temperatures requires a knowledge of data concerning the heat capacity of elements and compounds in the solid, liquid and gaseous states, as well as of their latent heats of fusion and vaporization, the next instalment of these calculations will supply these data as far as they are known, and discuss a number of applications of these principles to various metallurgical processes.

In order to apply the principles explained in the preceding discussion, two sets of data are necessary; first, the thermochemical data, such as are ordinarily obtained by laboratory experiments at laboratory temperatures; second, physical data concerning the specific heats and latent heats of fusion, and volatilization of elements and compounds. The first have been given, at least for all important compounds met with in metallurgy, in a previous **place (p. 18),** the latter will now be discussed and the data presented as far as they have been determined.

Specific Heats of the Elements.

Dulong and Petit's law announces the fact that the specific heat of atomic weight of a solid metal is nearly constant, the value varying between 6 and 7, and averaging 6.4. This generalization was made chiefly upon the basis of the specific heats of the metals, as determined in the range 100° C. to 10° or 15° C., such as in Regnault's accurate experiments. About the only notable exceptions to this rule are carbon, boron and silicon, and it has been naively remarked by more modern physicists that these exceptions to the rule disappear if we find the specific heat of these three elements at high temperatures, that, for instance, the specific heat of carbon above 1000° C. is 0.5. making its atomic specific heat $0.5 \times 12 = 6$, and therefore the exceptions to the rule are all accounted for. Now, the rule is an important one, and has done good service, but the exceptions just noted and their behavior at high temperatures really prove that the rule must be made more general, or else

abandoned altogether. The fact is, that the specific heats of almost all the solid elements increase with the temperature at a rate equal to an increase of about 0.04 per cent. of their value for each degree centigrade, so that the atomic specific heat of the majority of the elements, which is about 6.4 at ordinary temperatures, becomes about 40 per cent. greater at 1000° C. for such elements as are not melted at that temperature. Therefore, while we may say that at ordinary temperatures the specific heat of atomic weight of a solid element is 6.4, and its specific heat per unit of weight is 6.4, divided by the atomic weight, yet it will be more accurate, if actual determinations have not been made, to assume that the actual specific heat increases 0.04 per cent. for every degree rise in temperature, and mean specific heat to zero half that fast.

The specific heat in the liquid state has not been determined for many elements. It is in general higher than the specific heat of the solid at ordinary temperatures; in fact, it appears to be more nearly equal to the specific heat of the solid element just before fusion, and may be so assumed if no determinations have been made. It is found, furthermore, not to change perceptibly with rise of temperature, so that it may be assumed constant.

The specific heat of the gaseous elements has been determined only for those which are gaseous at low temperatures. For the metals which, as far as known, have monatomic vapors, *i.e.*, vapors in which the atoms exist alone and uncoupled with each other, the specific heat of atomic weight, occupying 22.22 cubic meters at standard conditions, should be theoretically 5.0 Calories at constant pressure, or 0.225 per cubic meter. We may thus estimate the specific heat of metallic vapors which have not been determined.

Latent Heats of Fusion of the Elements.

The passage from the solid to the liquid state is in all cases accompanied by an absorption of heat, which in amount varies from one or two Calories up to 100 Calories per unit of weight. This quantity has been most frequently determined by finding calorimetrically how much heat is given out by unit weight of the melted element just at its setting point, in cooling to

ordinary temperatures, and subtracting from this the heat in unit weight of the solid substance at the melting point, as determined most accurately by exterpolating the value of mean specific heat of the solid up to the melting point. In this manner the latent heat of fusion for a number of elements has been directly determined.

If a crucible full of melted metal is allowed to cool, the temperature falls regularly until the melting point is reached, and then stays constant, or nearly so, for some time, while the metal is setting. A comparison of the rate of cooling before and after setting, with the length of time during which the temperature was constant, gives the relative value of the latent heat of fusion in terms of the specific heat of the melted metal and of the solid metal near to the melting point.

While the latent heat of fusion per unit weight shows no perceptible regularities, it is found that as soon as the latent heat of fusion is expressed per atomic weight of the element (analogous to specific heat of atomic weight) that notable regularities appear. The elements with high melting points have high atomic heats of fusion, and *vice versa*, so that if the elements are arranged in the order of their melting points their latent heats of fusion per atomic weight of each are in the same order, and very nearly proportionately so. If, for instance, a chart or diagram is made, using the melting points as abscissas, and latent heats of fusion of atomic weights as ordinates, the latter will lie very nearly in a straight line. Numerically, if the melting points be expressed in degrees of absolute temperature (centigrade temperatures plus 273), the latent heats of fusion of atomic weights average about 2.1 times the temperature of the melting point. This rule may be used to predict an undetermined latent heat of fusion.

In addition to the above general rule, another one bearing on the same question was also discovered and applied by the writer. (See *Journal of the Franklin Institute*, May, 1897.) According to this observation, the continued product of the latent heat of fusion of atomic weight and the coefficient of expansion and the cube root of the atomic volume (atomic weight divided by specific gravity) is a constant. If the coefficient of linear expansion between 0° and 100° C. is used.

the constant is 0.095, or if the actual linear expansion of unit length from 0° to 100° C. is used, the constant is 9.5. This rule, applied to all elements whose latent heat of fusion is known, gives satisfactory agreements, and enables us therefore to predict the latent heat of fusion of nearly a dozen other elements for which the coefficient of expansion is known.

Latent Heats of Vaporization of the Elements.

This datum has been determined for but a very few elements. Some of the metalloids, like sulphur, phosphorous and arsenic, are known to become complex vapors immediately above their boiling point, corresponding to such formulæ as S^6, P^4, As^4; the metals, as far as they have been tested, pass into monatomic vapors, such as Na, K, Hg, Zn and Cd, in which each atom represents a molecule. In the latter cases the following generalization may be made: The latent heat of vaporization of atomic weight is proportional to the absolute temperatures of the boiling point at atmospheric pressure, and is numerically equal to about twenty-three times that temperature (twenty-one times, if the outer work of overcoming the atmospheric pressure be not included). From this rule it is possible to estimate the amount of heat necessary to vaporize any metal whose boiling point under atmospheric pressure is known.

Examples: The boiling point of carbon under atmospheric pressure is 3,700° C., and if its vapor is monatomic, the latent heat of vaporization is, for an atomic weight of carbon (C = 12), $23 \times (3700 + 273) = 92{,}080$ Calories, equal to 7,673 Calories per kilogram of carbon. If the vapor is diatomic, and its formula C^2, then the above latent heat is for twenty-four parts of carbon, and for one part by weight is 3,837 Calories. Other considerations, from thermochemistry, make the latter value the more probable one.

The boiling point of cadmium is 772° C., and its vapor is known to be monatomic, what is its latent heat of vaporization? The atomic weight being 112, the latent heat of vaporization of this quantity is $23 \times (772 + 273) = 24{,}035$ Calories, which is 215 Calories per kilogram.

In making such calculations it must be strictly observed that the boiling point *under atmospheric pressure* is to be used, and not any temperature at which vapors may appear at partial

tensions which may be only small fractions of atmospheric pressure.

Thermophysics of the Elements.

Having laid down the laws and the empirical rules which appear to govern these phenomena, we will now discuss the data for the common elements, giving both what is known and what may be assumed as probably true wherever actual determinations have not been made. The elements will be taken up in the order of their atomic weights,—the only scientifically logical order.

In all cases, the actually measured *mean* specific heats, Sm, will be given. In the case of gases, these will be the mean specific heats under constant pressure; if they are desired under constant volume the amount of outer work must be calculated in Calories (two Calories per degree for a molecular weight of a gas, 0.09 Calories per degree for 1 cubic meter, and 0.09÷ weight of 1 cubic meter for a kilogram of gas), and subtracted from the specific heat at constant pressure. The specific heat of 1 cubic foot is, in pound Calories, the specific heat per cubic meter divided by 35.32 and multiplied by 2.204, or, in brief, multiplied by 0.0624; in British thermal units it will be the same as in pound Calories, since t is then Fahrenheit degrees.

If, from the data given, it is desired to find the mean specific heat between any two temperatures, t and t′, instead of the mean specific heat from t to 0°, as given directly by the formula, it need only be observed that Sm from t′ to t is obtainable by finding Sm from 0° to (t′+t). If, for instance, Sm (o to t) = 0.303+0.000027t, then Sm (t to t′) = 0.303+ 0.000027 (t′+t). Furthermore, if the actual specific heat at any temperature t is desired, it is equal to the mean specific heat from 0° to 2t; *e.g.*, in the above cases, S (at any temperature t) = 0.303+0.000027 (2t) = 0.303+0.000054 (t).

Temperatures will be always given and represented in centigrade degrees, except where the specific heat is given in British thermal units, in which case t represents, of course, Fahrenheit degrees, and will also be printed in italics, *t*, to further distinguish it from t in centigrade degrees. Absolute temperatures, if used, will be designated as T, and are equal to t+273.

The vapor tensions of all the elements are expressed in the form $\log p = -\frac{A}{T}+B$, where p is used in millimeters of mercury, T is the corresponding temperature in absolute measure (K°), and A and B are constants for the elements in question, which can be found if merely two values of p and T are known. The latent heat of vaporization of molecular volume is, thermodynamically, 4.57A. B is found nearly constant for all elements, averaging 7.9 to 8.4 in the case of the liquid element and 8.85 for the solid element. If only one value of p and T are known, then B is assumed either 7.9 for elements of low boiling point or 8.4 for elements of high boiling point. A little study of the question will show that these values correspond to using 23 or 25.1 for Trouton's constant (KT) expressing the latent heat of vaporization of molecular volume at p=760 mm. (A/T=Trouton's constant/4.57). The vapor tension at the melting point is calculated by putting T=M. P., at which point the liquid and solid have the same vapor tension. This gives one value of p and T in the analogous formula for the solid state, $(\log. p = -\frac{A'}{T}+B')$, where A′ can be calculated from A and the latent heat of fusion, and B′ thus becomes known. The vapor tension down to 0° C. is then calculated from this formula.

Hydrogen.

From the experiments of Mallard and LeChatelier we deduce:

Sm (0−t)	1 kilogram (up to 2000° C.)	=3.370+0.0003t	Calories.
	1 pound (up to 2000° C.)	=3.370+0.0003t	pound Calories.
	1 pound (up to 3600° F.)	=3.370+0.00017*t*	B. T. U.
	1 cu. meter (up to 2000° C.)	=0.303+0.000027t	Calories.
	1. cu. foot (up to 2000° C.)	=0.0189+0.0000017t	pound Calories.
	1 cu. foot (up to 3600° F.)	=0.0189+0.0000009*t*	B. T. U.

For higher temperatures, such as electric furnace heats be-

tween 2000° and 4000° C. (3600° to 7200° F.), Berthelot and Vielle have made experiments which give us:

Sm (0—t)	1 kilogram	= 2.75 +0.0008t Calories.
	1 pound	= 2.75 +0.0008t pound Cal.
	1 pound	= 2.75 +0.00044*t* B. T. U.
	1 cubic meter	= 0.2575+0.000072t Calories.
	1 cubic foot	= 0.0161+0.0000045t pound Cal.
	1 cubic foot	= 0.0161+0.0000025*t* B. T. U.

Lithium.

Sm (0—t)	= 0.7895+0.0024t+ 0.0000063t^2 (Bernini).
S (at M. P. = 179°)	= 2.255.
Q (solid, at M. P.)	= 254 Cal.
L. H. Fusion	= 136 Cal. (calculated by 2.1 T rule).
	= 173 Cal. (calculated by second rule)
Q (liquid, at M. P.)	= 390 Cal. (calculated).
S (liquid)	= 2.255 (assumed).
Q (liquid at B. P. $_{760}$ =1450°)	= 3483 Cal. (calculated).
L. H. Vaporization (1450°)	= 5660 Cal. (Trouton's rule, K = 23).
Q (vapor; 1450°)	= 9140 Cal. (calculated).
S (vapor) per cubic meter	= 0.225 (assumed).
per kilo	= 0.714 (calculated).

Vapor tension, liquid : $\log p = -\frac{8690}{T} + 7.92$

(B = 7.92, assumed).

at M. P. $= 4.9 \times 10^{-12}$ mm. (calculated).

solid: $\log p = -\frac{8900}{T} + 8.38.$

at 0° C. $= 6.0 \times 10^{-25}$ mm. (calculated).

Beryllium (Glucinum).

Sm (0—t) = 0.38+0.0004t (Nilson & Pettersson).
S (at M. P. = 1430°) = 1.52.
Q (solid, at M. P.) = 1358 Cal.

L. H. Fusion = 400 cal. (calculated by 2.1 T rule).
Q (liquid, at M. P.) = 1758 Cal.
S (liquid) = 1.52 (assumed).

BORON.

Sm (0—t) (t under 233°) $= 0.22 + 0.00035t$ (Weber).
S (solid, at 500°) = 0.57 (by extension of above formula).
S (solid, above 500°) = 0.57 (assumed to remain constant).*
Sm (0—t) (t over 500°) $= 0.57 - \frac{88}{t}$.
Q (solid, at M. P. = 2500°) = 1337 Cal. (calculated).
L. H. Fusion = 265 Cal. (calculated by 2.1 T rule, and molecule B_2).
Q (liquid, at M. P.) = 1602 Cal (calculated).
S (liquid) = 0.57 (assumed).
Q (liquid at B. $P._{760}$ = 3700°) = 2285 Cal.
L. H. Vaporization (3700°) = 4155 Cal. (Trouton's rule, K = 23, and molecule B_2).
Q (vapor, 3700°) = 6440 Cal.
S (vapor) per cubic meter = 0.315 (assumed for B_2).
per kilo = 0.318 (calculated).

Vapor tension, liquid: $\log p = -\frac{19{,}950}{T} + 7.92$ (B = 7.92 assumed).
at M. P. = 5 mm.
solid: $\log p = -\frac{21{,}230}{T} + 8.36$.
at 0° C. $= 3.9 \times 10^{-70}$ mm. (calculated).

CARBON.

(*Amorphous and Graphitic.*)

Sm (0°—t°) (up to 250°) $= 0.1567 + 0.00036t$.
(0°—t°) (250°—1000°) $= 0.2142 + 0.000166t$.
S at 1000° = 0.528 (Violle); 0.546 (Weber).
Q at 1000° = 380 Cal.
Sm (0—t) (t over 1000°) $= 0.4430 + 0.0000425t - \frac{106.5}{t}$ (Violle).

*This figure would give atomic specific heat = 6.27, and we assume this constancy by analogy with similar behavior of carbon.

Q (0—t) (t over 1000°) $= 0.4430t+0.0000425t^2-106.5.$
Q (solid) (at B. P.$_{760}$ = 3700°) = 2114 Cal.
L. H. Sublimation (3700°) = 4140 Cal. (Richard's rule, K = 2.1, and Trouton's rule, K = 23; for C_2).
Q (vapor) (3700°) = 6254.
S (solid, at M. P. = 4400°) = 0.777 (Violle's equation).
S (vapor) per cubic meter = 0.315 (assumed).
per kilo = 0.292 (calculated for C_2).
Q (solid) (at M. P. 4400°) = 2666 Cal. (by Violle's equation).
L. H. Fusion (4400°) = 409 Cal. (by 2.1 T rule for C_2).
= 396 Cal. (by second rule, for C_2).
Q (liquid) (4400^0) = 3066 Cal. (calculated).
S (liquid) = 0.777 (assumed).
Q (vapor) (4400°) = 6806 Cal. (calculated).

Vapor tension, solid: $\log p = -\frac{24{,}300}{T}+9.0$ (B′ = 9.0, assumed).

at M. P. = 6310 mm. = 8.3 atmospheres.

liquid: $\log p = -\frac{22{,}195}{T}+8.5.$

at 0°C. $= 1\times10^{-80}$ mm. (calculated).

Nitrogen.

Sm (0—t) 1 kilogram (up to 2000° C.) $= 0.2405+0.0000214t$ Cal.
1 pound (up to 2000° C.) $= 0.2405+0.0000214t$ pound Cal.
1 pound (up to 3600° F.) $= 0.2405+0.0000119t$ B. T. U.
1 cubic meter (up to 2000° C.) $= 0.303+0.000027t$ Cal.
1 cu. foot (up to 2000° C.) $= 0.0189+0.0000017t$ pound Cal.
1 cu. foot (up to 3600° F.) $= 0.0189+0.0000009t$ B. T. U.

For temperatures between 2000° and 4000° C. the following are the values of the mean specific heats to zero:

Sm (0—t) 1 kilogram $= 0.2044+0.000057t$ Cal.
1 pound $= 0.2044+0.000057t$ pound Cal.

1 pound = $0.2044+0.000032t$ B. T. U.
1 cubic meter = $0.2575+0.000072$t Cal.
1 cubic foot = $0.1601+0.0000045$t pound Cal.
1 cubic foot = $0.0161+0.0000025t$ B. T. U.

OXYGEN.

Sm (0—t) 1 kilogram (up to 2000° C.) = $0.2104+0.0000187$t Cal.
1 pound (up to 2000° C.) = $0.2104+0.0000187$t pound Cal.
1 pound (up to 3600° F.) = $0.2104+0.0000104t$ B. T. U.
1 cu. meter (up to 2000° C.) = $0.303+0.000027$t Cal.
1 cu. foot (up to 2000° C.) = $0.0189+0.0000017$t pound Cal.
1 cu. foot (up to 3600° F.) = $0.0189+0.0000009t$ B. T. U.
Sm (0—t) 1 cu. meter (2000°−4000°C) = $0.2575+0.000072$t Cal.
1 cu. foot (2000°−4000° C.) = $0.0161+0.0000045$t pound Cal.
1 cu. foot (3600°−7200° F.) = $0.0161+0.0000025t$ B. T. U.
1 kilogram (2000°−4000° C) = $0.1788+0.00005$t Cal.
1 pound (2000°−4000° C.) = $0.1788+0.00005$t pound Cal.
1 pound (3600°−7200° F.) = $0.1788+0.00003$t B. T. U.

SODIUM.

Sm (0—t) = $0.2932+0.00019$t (Bernini).
Q (solid, at M. P. = 98°) = 30.6 Cal. (by formula).
L. H. Fusion = 27.2 (Rengade).
Q (liquid, at M. P.) = 57.8 Cal.
S (liquid, 98°—100°) = 0.333 (Bernini).
Q (liquid at B. $P._{760}$ = 877°) = 317 Cal. (calculated).
L. H. Vaporization (877°) = 905 Cal. (from vapor tension constants).
Q (vapor, at 877°) = 1222 Cal.
S (vapor) for cubic meter = 0.225 (assumed).
per kilo = 0.218 (calculated).

Vapor tension, liquid: $\log p = -\frac{4565}{T} + 6.85$ (from Gebhardt's data)

at M. P. $= 3.55 \times 10^{-6}$ mm. (calculated).

solid: $\log. p = -\frac{4700}{T} + 7.30.$

at 0° C. $= 8.1 \times 10^{-9}$ mm. (calculated).

Magnesium.

Sm (0—t°)	$= 0.2372 + 0.000093t + 0.0000000685t^2$ (Stücker).
Q (solid, at M. P. = 650°)	= 212 Cal. (by formula).
L. H. Fusion	= 70 Cal. (Roos).
Q (liquid, at M. P.)	= 282 Cal.
S (liquid)	= 0.445 (assumed; same as solid at M. P.).
Q (liquid, at B. $P._{760}$ = 1120°)	= 491 Cal. (calculated).
L. H. Vaporization (1120°)	= 1443 Cal. (Trouton's rule, K = 25.2).
Q (vapor, at 1120°)	= 1934 Cal.
S (vapor) per cubic meter	= 0.225 (assumed).
kilo	= 0.208 (calculated).
Vapor tension, liquid : log p	$= -\frac{7690}{T} + 8.4$ (constants from Trouton's rule).
at M. P.	= 1.15 mm. (calculated).
solid : log p	$= -\frac{8060}{T} + 8.81.$
at 0° C.	$= 5.25 \times 10^{-20}$ mm. (calculated).

Aluminium.

Sm(0—t°)	= 0.2220+0.00005t (Richards).
Q (solid, at M. P. = 657°)	= 167.4 Cal. (from formula).
L. H. Fusion	= 90.9 Cal. (Richards).
Q (liquid, at M. P.)	= 258.3 Cal. (Richards).
S (liquid)	= 0.308 (Pionchon).
Q (liquid, at B. $P._{760}$ = 2200°)	= 733.5 Cal. (calculated).
L. H. Vaporization (2200°)	= 2305 Cal. (Trouton's rule, K = 25.2).

Q (vapor, at 2200°) = 3039 Cal.
S (vapor) per cubic meter = 0.225 (assumed).
kilo = 0.185 (calculated).
Vapor tension, liquid : $\log p = -\frac{13,650}{T} + 8.4$ (constants from Trouton's rule).
at M. P. = 5.25×10^{-7} mm. (calculated).
solid : $\log p = -\frac{14,190}{T} + 8.98$.
at 0° C. = 1.0×10^{-43} mm. (calculated).

SILICON.

Sm(0—t°)(up to 234°) = 0.17+0.00007t (Weber).
Q (solid, at M. P. = 1430°) = 386 Cal. (by extension of formula).
L. H. Fusion = 128 Cal. (by 2.1 T rule).
= 108 Cal. (by second rule).
Q (liquid, at 1430°) = 494 Cal.
S (liquid) = 0.37 (assumed, same as solid at M. P.).
Q (liquid, at B. $P._{760}$ = 2300°) = 816 Cal. calculated).
L. H. Vaporization (2300°) = 1153 Cal. (Trouton's rule, K = 25.2, vapor = Si_2).
Q (vapor, at 2300°) = 1969 Cal.
S (vapor) per cubic meter = 0.315 (assumed, for Si_2).
per kilo = 0.125 (calculated).
Vapor tension, liquid : $\log p = -\frac{14,200}{T} + 8.4$ (constants from Trouton's rule).
at M. P. = 1.32 mm. (calculated).
solid : $\log p = -\frac{15,530}{T} + 9.00$.
at 0° C. = 8×10^{-47} mm. (calculated).

PHOSPHORUS.

Sm(−20 to 7°) = 0.1788.
Q (solid, at M. P. = 44°) = 8 Cal.
L. H. Fusion (44°) = 5 Cal. (Person).
Q (liquid, at 44°) = 13 Cal.
S (liquid, 44° to 98°) = 0.205.
Q (liquid at B. $P._{760}$ = 287°) = 63 Cal.

L. H. Vaporization (287°) = 130 Cal.
Q (vapor, at 287°) = 193 Cal.
S (vapor) per cubic meter = 0.405 (assumed, for P_3).
per kilo = 0.097 (calculated).

Vapor Tension, liquid : $\log p = -\frac{2160}{T} + 7.0.$
at M. P. = 1.63 mm.
solid : $\log p = -\frac{2260}{T} + 7.34.$
at 0° C. = 0.115 mm.

Sulfur.

Sm(15°—97°) = 0.18 (Regnault).
Q(solid, at M. P. = 113°) = 20 Cal.
L. H. Fusion = 9.4 (Person).
Q (liquid, at M. P.) = 29.4 Cal.
Sm(0—t°)(liquid, 114°—445°) = $0.338 + 0.000187t - 0.00000058t^2$.
Q (liquid at B. $P._{760}$ = 444°.5) = 126 Cal.
L. H. Vaporization (444°.5) = 72 Cal.
Q (vapor, at 444°.5) = 198 Cal.
S (vapor) per cubic meter = 0.855 for S_8, close to 445°.
per cubic meter = 0.674 for S_6, up to 500°.
per cubic meter = 0.315 for S_2, over 800°.
per kilo = 0.074 for S_8, close to 445°.
= 0.078 for S_6, up to 500°.
= 0.109 for S_3, over 800°.

Vapor tension, liquid : $\log p = -\frac{3745}{T} + 8.1.$
at M. P. = 0.028 mm.
solid : $\log p = -\frac{4140}{T} + 9.15.$
at 0° C. = 1×10^{-6} mm.

Chlorine.

Sm (gas) per cubic meter = 0.40 (13°—202°) (Regnault).
per kilo = 0.1241 (Regnault).

Potassium.

Sm(0—t°)	= 0.1858+0.00008t (Bernini).
Q (solid, at M. P. = 60°)	= 11.4 Cal.
L. H. Fusion	= 13.6 Cal. (Bernini).
Q (liquid, at M. P.)	= 25.0 Cal.
Sm (liquid) (0—t°)	= 0.1422+0.00067t (Rengade).
Q (liquid, at B. $P._{760}$ = 757°)	= 181.5 Cal.
L. H. Vaporization (757°)	= 607 Cal. (Trouton's rule, K = 23).
Q (vapor, at 757°)	= 789 Cal.
S (vapor) per cubic meter	= 0.225 (assumed).
per kilo	= 0.128 (calculated).

Vapor Tension, liquid : $\log p = -\frac{5190}{T}+7.92$ (constants from Trouton's rule).

at M. P. $= 2.25\times10^{-8}$ mm.

solid : $\log p = -\frac{5300}{T}+8.26.$

at 0° C. $= 7.1\times10^{-12}$ mm.

Calcium.

Sm(0°—100°)	= 0.1704 (Bunsen).
Q (solid, at M. P. = 800°)	= 136.3 Cal.
L. H. Fusion	= 56.3 Cal. (calculated by 2.1 T rule).
Q (liquid, at M. P.)	= 192.6.

Titanium.

S (solid, at 0°)	= 0.0978 (Nilson and Pettersson).
Sm (0—t°)	= 0.0978+0.0000035t (assuming atomic specific heat = 10 at M. P.).
Q (solid, at M. P. = 1795°)	= 187 Cal. (from above formula).
L. H. Fusion	= 90 Cal. (from 2.1 T rule).
Q (liquid, at M. P.)	= 277 Cal.
S (liquid)	= 0.2084 (assumed, same as solid at M. P.).
Q (liquid, at B. $P._{760}$ = 2475°)	= 319 Cal.

L. H. Vaporization (2475°) = 143 Cal. (from Trouton's rule, K = 25).

Q (vapor, at 2475°) = 462 Cal.

S (vapor) per cubic meter = 0.225 (assumed).

per kilo = 0.104 (calculated).

Vapor tension, liquid : $\log p = -\frac{15{,}170}{T} + 8.4.$

at M. P. = 11.75 mm.

solid : $\log p = -\frac{16{,}090}{T} + 8.85.$

at 0° C. $= 8.3 \times 10^{-49}$ mm.

VANADIUM.

Sm (0—t°) = 0.105+0.00003t.

Q (solid, at M. P. = 1710°) = 267 Cal.

L. H. Fusion = 82 Cal. (by 2.1 T rule).

Q (liquid, at M. P.) = 349 Cal.

S (liquid) = 0.208 (assumed, same as solid at M. P.).

CHROMIUM.

Sm (0—t°) (to 600°) $= 0.1039 + 0.00000008t^2$ (Adler).

Q (solid, at M. P. = 1489°) = 352 Cal.

L. H. Fusion = 71 Cal. (calculated by 2.1 T (rule).

Q (liquid, at M. P.) = 423 Cal.

S (liquid) = 0.24 (estimated).

Q (liquid at B. $P._{760}$ = 2200°) = 594 Cal.

L. H. Vaporization (at 2200°) = 1197 Cal. (Trouton's rule, K = 25.1).

Q (vapor, at 2200°) = 1791 Cal.

S (vapor), per cubic meter = 0.225 (assumed).

per kilo = 0.096

Vapor tension, liquid : $\log p. = -\frac{13{,}650}{T} + 8.4$ (constants from Trouton's rule, K = 25.1).

at M. P. = 4.47 mm.

solid : $\log p. = -\frac{14{,}460}{T} + 8.86.$

at 0° C. $= 7.8 \times 10^{-45}$ mm.

MANGANESE.

Sm (0—t°) = 0.1088+0.000103t.
Q (solid, at M. P. = 1207°) = 281 Cal.
L. H. Fusion = 43 Cal. (calculated by second rule.)
Q (liquid, at M. P.) = 324 Cal.
S (liquid) = 0.357 (assumed from S solid at M. P.).
Q (liquid at B. $P._{760}$ = 1900°) = 572 Cal.
L. H. Vaporization (1900°) = 995 Cal. (Trouton's rule, K = 25.1).
Q (vapor, at 1900°) = 1567 Cal.
S (vapor) per cubic meter = 0.225 (assumed).
per kilo. = 0.091 (calculated).

Vapor tension, liquid : $\log p = -\frac{11{,}995}{T} + 8.4$ (Constants from Trouton's rule, K = 25.1).
at M. P. = 1.98 mm. Hg.
solid : $\log p. = -\frac{12{,}650}{T} + 8.85.$
at 0° C. = 3.2×10^{-38} mm. Hg.

IRON.

Sm(0—t°) up to 660° = 0.11012+0.000025t+ 0.0000000547t^2 (Pionchon; also Oberhoffer).
Q at 660° = 96.1 Cal.
Q at 750° = 125.6 Cal.
L. H. Change of state (730°) = 5.3 Cal. (Pionchon); 5.0 (Leschtschenko).
S above 750° = 0.1675 (approximately constant.)
Q (0—t°) t = 750° to 1500° = 0.1675t − 51 Cal.
L. H. Change of state (900°) = 6.0 Cal. (Pionchon); 6.1 (Leschtschenko).
Q (solid, at M. P. = 1535°) = 256 Cal.
L. H. Fusion = 66 Cal. (calculated by 2.1 T rule).
= 69 Cal. (calculated by second rule).
(4.3% C.) = 59 Cal. (Schmidt).

Q (liquid, at 1535°) = 322 Cal.
S (liquid) = 0.20 (estimated).
Q (liquid at B. $P._{760}$ = 2450°) = 505 Cal.
L. H. Vaporization (2450°) = 1224 Cal. (Trouton's rule, K = 25.1).
S (vapor) per cubic meter = 0.225 (assumed).
per kilo. = 0.089 (calculated).

Vapor tension, liquid : $\log p. = -\frac{15{,}030}{T} + 8.4$ (Constants from Trouton's rule, K = 25.1).
at M. P. = 1.20 mm. Hg.
solid : $\log p. = -\frac{15{,}840}{T} + 8.84.$
= at 0° C. $= 6.9 \times 10^{-50}$ mm.

NICKEL.

Sm (0—t°) up to 230° = 0.10836+0.00002233t (Pionchon).
L. H. Change of State = 4.64 Cal., 230° to 400°, (Pionchon).
= 3.11 Cal. 363° (Leschtschenko).
Sm (0—t°) t = 440° to 1050° $= 0.099+0.00003375t+\frac{6.55}{t}$ (Pionchon).
Q (solid, at M. P. = 1450°) = 221 Cal.
L. H. Fusion = 68 Cal. (calculated by second rule).
Q (liquid, at 1450°) = 289 Cal.
S (liquid) = 0.197 (estimated).
Q (liquid, at B. $P._{760}$ = 2150°) = 427 Cal.
L. H. Vaporization (2150°) = 1042 Cal. (Trouton's rule, K= 25.1).
S (vapor) per cubic meter = 0.225 (assumed).
per kilo = 0.086 (calculated).

Vapor tension, liquid : $\log p. = -\frac{13{,}375}{T} + 8.4$ (Constants from Trouton's rule, K=25.1).
at M. P. = 4.36 mm. Hg.
solid : $\log p. = -\frac{14{,}245}{T} + 8.9.$
at 0° C. $= 5.25 \times 10^{-44}$ mm. Hg.

COBALT.

Sm (0—t°) up to 900° = $0.10584+0.00002287t+0.000000022t^2$ (Pionchon).

Sm (0—t°)t over 900° = $0.124+0.00004t-\frac{14.8}{t}$ (Pionchon).

Q (solid, at M. P. = 1490°) = 259 Cal. (extension of above formula).

L. H. Fusion = 68 Cal. (calculated by second rule).

Q (liquid, at 1490°) = 327 Cal.

S (liquid) = 0.243 (assumed, same as solid at M. P.).

COPPER.

Sm (0—t) = $0.0939+0.00001778t$ (Frazier and Richards).

Q (solid, at M. P. = 1083°) = 118.7 Cal.

L. H. Fusion = 43.3 Cal. (Richards).

Q (liquid, at M. P.) = 162.0 Cal. (Frazier & Richards).

S (liquid) = 0.156 (Glaser).

Q (liquid, at B. $P._{760}$ = 2310°) = 353 Cal.

L. H. Vaporization (2310°) = 1087 Cal. (calculated, from vapor tension curve).

Q (vapor, at 2310°) = 1440 Cal.

S (vapor) per cubic meter = 0.225 (assumed).

per kilo = 0.079 (calculated).

Vapor tension, liquid : $\log p. = -\frac{15{,}160}{T}+8.75$ (from Greenwood's data).

at M. P. = 3.5×10^{-3} mm. Hg.

solid : $\log p. = -\frac{15{,}765}{T}+9.17.$

at 0° C. = 2.6×10^{-49} mm. Hg.

ZINC.

Sm (0—t°) = $0.0906+0.000044t$.

Q (solid, at M. P. = 419°) = 45.2 Cal.

L. H. Fusion = 22.6 Cal. (Richards).
Q (liquid, at M. P.) = 67.8 Cal.
S (liquid) = 0.179 (Glaser).
Q (liquid, at B. $P._{760}$ = 930°) = 159 Cal.
L. H. Vaporization (930°) = 446 Cal. (calculated from vapor tension curve).
Q (vapor at 930°) = 605 Cal.
S (vapor) per cubic meter = 0.225 (assumed).
per kilo = 0.077 (calculated).

Vapor tension, liquid : $\log p = -\frac{6365}{T} + 8.17$ (from various observations).

at M. P. $= 9.3 \times 10^{-2}$ mm. Hg.

solid : $\log p. = -\frac{6685}{T} + 8.63.$

at 0° C. $= 1.03 \times 10^{-16}$ mm. Hg.

Gallium.

Sm (12° to 23°) = 0.079 (Berthelot).
Q (solid, at M. P. = 30°) = 2.4 Cal.
L. H. Fusion = 19.3 Cal. (Berthelot).
Q (liquid, at M. P.) = 21.7 Cal.
S (liquid, 30°—119°) = 0.084 (Berthelot).

Arsenic.

Sm (21° to 65°) amorphous = 0.0758 (Bettendorf and Wüllner).
crystalline = 0.083 (Bettendorf and Wüllner).
Q (solid, at S. $P._{760}$ = 616°) = 47 Cal.
L. H. Sublimation (616°) = 114 Cal. (calculated from vapor tension curve, for As_3).
Q (vapor, at 616°) = 161 Cal.
S (vapor) per cubic meter = 0.405 (assumed for As_3).
per kilo = 0.040 (calculated).

Q solid, at M. P. = 827°) = 63 Cal.
L. H. Fusion (827°) = 10 Cal.
Q (liquid at 827°) = 73 Cal.
L. H. Vaporization, 827°) = 104 Cal.
Q (vapor, at 827°) = 177 Cal.

} under 10,000 mm. pressure.

Vapor tension, solid : $\log p. = -\frac{5610}{T} + 9.10$ (from experimental data).

at M. P. = 10,000 mm. Hg.

liquid : $\log p. = -\frac{5115}{T} + 8.65$ (from experimental data.)

at 0° C. $= 2.8 \times 10^{-21}$ mm. Hg.

SELENIUM.

Sm (60°—200°) = 0.084 (Bettendorf and Wüllner).
Q (solid, at M. P. = 217°) = 18 Cal.
L. H. Fusion = 4 Cal.
Q (liquid at M. P.) = 22 Cal.
S (liquid) = 0.12 (assumed).
Q (liquid, at B. $P._{760}$ = 690°) = 79 Cal.
L. H. Vaporization (690°) = 97 Cal. (calculated from vapor tension curve, for Se_3).
Q (vapor, at 690°) = 176 Cal.
S (vapor) per cubic meter = 0.405 (assumed for Se_3).
per kilo = 0.038 (calculated).

Vapor tension, liquid : $\log p = -\frac{5025}{T} + 8.10$ (from experimental data).

at M. P. = 0.71 mm. Hg.

solid : $\log. p = -\frac{5250}{T} + 8.56$

at 0° C. $= 2.1 \times 10^{-11}$ mm. Hg.

BROMINE.

Q (solid, at M. P. = −7°) = −16.9 Cal.
L. H. Fusion (−7°) = 16.2 Cal. (Regnault).
Q (liquid, at M. P.) = −0.7 Cal.
Sm (liquid, −6° to +58°) = 0.105+0.0011t
Q (liquid, at B. $P._{760}$ = 58°) = 10 Cal.
L. H. Vaporization (58°) = 43.7 Cal. (Berthelot and Ogier).
Q (vapor, at 58°) = 53.7 Cal.
S (vapor) per cubic meter = 0.40
per kilo = 0.0555 (Regnault).

Vapor tension, liquid : $\log p = -\frac{1635}{T} + 7.8$ (from experimental data).

at M. P. = 45 mm. Hg.
at 0° C. = 66 mm. Hg.

Rubidium.

Sm (20° to 35°) = 0.0792+0.00001t (Deusz).
Q (solid, at M. P. = 38°) = 3 Cal.
L. H. Fusion = 6 Cal. (E. Duess).
Q (liquid, at 38°) = 9 Cal.
S (liquid) = 0.080 (assumed).
Q (liquid, at B. $P._{760}$ = 696°) = 62 Cal.
L. H. Vaporization (696°) = 261 Cal. (from Trouton's rule; K = 23).
Q (vapor, at 696°) = 323 Cal.
S (vapor) per cubic meter = 0.225 (assumed).
per kilo = 0.059 (calculated).

Vapor tension, liquid : $\log p = -\frac{4890}{T}+7.90$ (constants from Trouton's rule; K = 23).
at M. P. $= 1.5\times10^{-8}$ mm. Hg.
solid : $\log p = -\frac{5040}{T}+8.28$.
at 0° C. $= 6.7\times10^{-11}$ mm. Hg.

Strontium.

Sm (0°—100°) = 0.0735 (assumed by Dulong and Petit's Law).
Q (solid, at M. P. = 800°) = 59 Cal.
L. H. Fusion = 26 Cal. (calculated by 2.1 T rule).
Q (liquid, at 800°) = 85 Cal.
S (liquid) = 0.092 (assumed, from at. sp. heat = 8.0).

Zirconium.

Sm (0°—100°) = 0.0662 (Mixter and Dana).
Q (solid, at M. P. = 2350°) = 155 Cal.
L. H. Fusion = 61 Cal. (calculated by 2.1 T rule).
Q (liquid, at 2350°) = 216 Cal.
S (liquid) = 0.11 (assumed, from at. sp. heat = 10).

Columbium (Niobium).

Sm (0—100°) = 0.068 (assumed, from Dulong and Petit's Law).
Q (solid, at M. P. = 1950°) = 133 Cal.

L. H. Fusion = 50 Cal. (calculated by 2.1 T rule).
Q (liquid, at 1950°) = 183 Cal.
S (liquid) = 0.107 (assumed from at. sp. heat = 10).

MOLYBDENUM.

Sm (0°—t°) = 0.0655+0.00002t (Defacqz and (Guichard).
Q (solid, at M. P. = 2500°) = 289 Cal.
L. H. Fusion = 61 Cal. (calculated by 2.1 T rule).
Q (liquid, at 2500°) = 350 Cal.
S (liquid) = 0.165 (assumed, from extension of formula for S (solid).
Q (liquid at B. $P._{760}$ = 3600°) = 522 Cal.
L. H. Vaporization (3600°) = 1015 Cal. (calculated from Trouton's rule; K = 25).
Q (vapor, at 3600°) = 1537 Cal.
S (vapor) per cubic meter = 0.225 (assumed).
per kilo = 0.052 (calculated).
Vapor tension, liquid : log p = $-\frac{21{,}380}{T}+8.4$ (constants from Trouton's rule, K = 25).
at M. P. = 4.9 mm. Hg.
solid : log p = $-\frac{22{,}650}{T}+8.85$.
at 0° C. = 7.6×10^{-75} mm. Hg.

RUTHENIUM.

Sm (0°—100°) = 0.0611 (Bunsen).
Sm (0°—t°) = 0.0601+0.00001t (function of t assumed).
Q (solid, at M. P. = 1950°) = 155 Cal. (extension of above formula).
L. H. Fusion = 46 Cal. (calculated by second rule).
Q (liquid, at M. P.) = 201 Cal.
S (liquid) = 0.099 (assumed same as solid at M. P.).
Q (liquid at B. $P._{760}$ = 2520°) = 257 Cal.
L. H. Vaporization = 689 Cal. (calculated from Trouton's rule, K = 25).

Q (vapor, at 2520°) = 946 Cal.
S (vapor) per cubic meter = 0.225 (assumed).
per kilo = 0.049 (calculated).
Vapor tension, liquid : $\log p = -\frac{15{,}420}{T} + 8.4$ (constants from Trouton's rule; K = 25).
at M. P. = 28.8 mm. Hg.
solid : $\log p = -\frac{16{,}450}{T} + 8.86$.
at 0° C. = 4×10^{-52} mm. Hg.

RHODIUM.

Sm (10°—97°) = 0.0580 (Regnault).
Sm (0°—t°) = 0.0574+0.00001t (function of t assumed).
Q (solid, at M. P. = 1970°) = 152 Cal.
L. H. Fusion = 53 Cal. (calculated by second rule).
Q (liquid, at M. P.) = 205 Cal.
S (liquid) = 0.097 (assumed same as solid at M. P.
Q (liquid at B. $P._{760}$ = 2500°) = 256 Cal.
L. H. Vaporization (2500°) = 677 Cal. (calculated from Trouton's rule, K = 25).
Q (vapor, at 2500°) = 933 Cal.
S (vapor) per cubic meter = 0.225 (assumed).
per kilo = 0.049 (calculated).
Vapor tension, liquid : $\log p = -\frac{15{,}300}{T} + 8.4$.
at M. P. = 38 mm. Hg.
solid : $\log p = -\frac{16{,}500}{T} + 8.94$.
at 0° = 3.2×10^{-52} mm. Hg.

PALLADIUM.

Sm (0°—t°) = 0.0582+0.00001t (Violle).
Q (solid, at M. P. = 1549°) = 110 Cal. (Violle).
L. H. Fusion = 36 Cal. (Violle).
Q (liquid, at M. P.) = 146 Cal. (Violle).
S (liquid) = 0.089 (assumed same as solid at M. P.).

Q (liquid, at B. $P._{760}$ = 2535°) = 238 Cal.
L. H. Vaporization (2535°) = 667 Cal. (calculated from Trouton's rule; K = 25).
Q (vapor, at 2535°) = 905 Cal.
S (vapor) per cubic meter = 0.225 (assumed).
per kilo = 0.047 (calculated).
Vapor tension, liquid : $\log p = -\frac{15{,}500}{T} + 8.4$ (constants from Trouton's rule, K = 25.1).
at M. P. $= 7.8 \times 10^{-1}$ mm. Hg.
solid : $\log p = -\frac{16{,}340}{T} + 8.85$
at 0° $= 1.4 \times 10^{-60}$ mm. Hg.

Silver.

Sm (0°—t°) up to 400° = 0.0555+0.00000943t (Pionchon).
over 400° = 0.05758+0.0000044t+ $0.000000006t^2$ (Pionchon).
Q (solid, at M. P. = 962°) = 64.8 Cal.
L. H. Fusion = 24.35 Cal. (Pionchon).
Q (liquid, at M. P.) = 89.15 Cal. (Pionchon).
S (liquid, 962° to 1020°) = 0.0748 (Pionchon).
Q (liquid at B. $P._{760}$ = 2040°) = 170 Cal.
L. H. Vaporization (2040°) = 490 Cal. (calculated from vapor tension data).
Q (vapor, at 2040°) = 660 Cal.
S (vapor) per cubic meter = 0.225 (assumed).
per kilo = 0.046 (calculated).
Vapor tension, liquid : $\log p. = -\frac{11{,}600}{T} + 7.9$ (from experimental data).
at M. P. $= 3.2 \times 10^{-2}$ mm. Hg.
solid : $\log p = -\frac{12{,}180}{T} + 8.36$.
at 0° C. $= 5.6 \times 10^{-37}$ mm. Hg.

Cadmium.

Sm (0°—t°) = 0.0546+0.000012t (Naccari).
Q (solid, at M. P. = 321°) = 18.8 Cal.
L. H. Fusion = 13.0 Cal. (Person).

Q (liquid, at M. P.) = 31.8 (Person).
S (liquid) = 0.0623 (calculated same as solid at M. P.).
Q (liquid, at B. $P._{760}$ = 778°) = 60.3 Cal.
L. H. Vaporization (778°) = 251 Cal. (calculated from vapor tension curve).
Q (vapor, at 778°) = 311 Cal.
S (vapor) per cubic meter = 0.225 (assumed).
per kilo. = 0.045 (calculated).
Vapor tension, liquid : $\log p = -\frac{6151}{T} + 8.74$ (from experimental data).
at M. P. $= 2.6\times10^{-2}$ mm.
solid : $\log p = -\frac{6470}{T} + 9.28$.
at 0° C. $= 3.8\times10^{-15}$ mm. Hg.

TIN.

Sm (0°—t°) = 0.0560+0.000044t (Bede, combined with Regnault.).
Q (solid, at M. P. = 232°) = 14.34 Cal.
L. H. Fusion = 13.82 Cal. (Richards).
Q (liquid, at M. P.) = 26.16 Cal. (Richards).
Sm (0°—t°)(t = 232° to 1000°) $= 0.06129 - 0.00001047t + 0.00000001035t^2 + \frac{14.37}{t}$ (Pionchion).
S (liquid) at t = 232° to 1000° $= 0.06129 - 0.00002094t + 0.00000003105t^2$ (Pionchon).
Q (liquid, at B. $P._{760}$ = 2250°) = 157 Cal.
L. H. Vaporization (2250°) = 538 Cal. (calculated from Trouton's rule, K = 25.1).
Q (vapor, at 2250°) = 695 Cal.
S (vapor) per cubic meter = 0.225 (assumed).
per kilo = 0.042 (calculated).
Vapor tension, liquid : $\log p = -\frac{13,930}{T} + 8.4$ (Constants from Trouton's rule, K = 25.1).
at M. P. $= 6.3\times10^{-20}$ mm. Hg.
solid : $\log p = -\frac{14,290}{T} + 9.1$.
at 0° C. $= 5.6\times10^{-44}$ mm. Hg.

ANTIMONY.

Sm (0°—t°)	= 0.04864+0.0000084t (Naccari).
Q (solid, at M. P. = 630°)	= 34 Cal.
L. H. Fusion	= 40.3 Cal. (Richards).
Q (liquid, at M. P.)	= 74.3 Cal. (Richards).
S (liquid, 632° to 830°)	= 0.0605 (Richards).
Q (liquid, at B. $P._{760}$ = 1500°)	= 127 Cal.
L. H. Vaporization (1500°)	= 124 Cal. (calculated from Trouton's rule for Sb_3, K = 25.1).
Q (vapor, at 1500°)	= 251 Cal.
S (vapor) per cubic meter	= 0.405 (assumed, for vapor = Sb_3).
per kilo	= 0.025 (calculated for Sb_3).
Vapor tension, liquid : log p	$= -\frac{9790}{T} + 8.4$ (constants from Trouton's rule, K = 25.1).
at M. P.	$= 3.55 \times 10^{-3}$ mm. Hg
solid : log p	$= -\frac{10{,}850}{T} + 9.58.$
at 0° C.	$= 6.5 \times 10^{-31}$ mm. Hg.

IODINE.

Sm (9°—98°)	= 0.05412 (Regnault).
Q (solid, at M. P. = 114°)	= 6.2 Cal.
L. H. Fusion	= 11.7 Cal. (Person).
Q (liquid, at M. P.)	= 17.9 Cal.
S (liquid)	= 0.0676 (assumed).
Q (liquid, at B. $P._{760}$ = 185°)	= 22.7 Cal.
L. H. Vaporization (185°)	= 23.95 Cal. (Fabre and Silbermann).
Q (vapor, at 185°)	= 46.65 Cal. per kg.
S (vapor) per kilo (206° to 377°)	= 0.034 (Strecker).
per cubic meter	= 0.389 (calculated).
per cu. meter (>1200°)	= 0.225 (assumed for I gas).
per kilo	= 0.039 (calculated).
L. H. Change of State (I_2 = 2I)	= 145 Cal. per kilo (calculated from vapor tension curve).
	= 1658 Cal. per cubic meter I_2.

Q (vapor, at 1200° = I vapor) = 226 Cal. per kilo.

Vapor tension, liquid : $\log p = -\frac{2390}{T} + 8.10$ (from experimental data).

at M. P. = 89 mm. Hg.

solid : $\log p = -\frac{3458}{T} + 10.43$.

at 0° = 2×10^{-2} mm. Hg.

TELLURIUM.

Sm (0°—455°) = 0.0613 (Richards).

Sm (0°—t°) = 0.0495+0.000026t (Richards).

Q (solid, at M. P. = 455°) = 27.3 Cal.

L. H. Fusion = 19.0 Cal. (Richards).

Q (liquid, at M. P.) = 46.3 Cal. (Richards).

S (liquid) = 0.0731 (calculated same as solid at M. P.)

Q (liquid at B. $P._{760}$ = 1390°) = 115 Cal.

L. H. Vaporization (1390)° = 166 Cal. (calculated by Trouton's rule for Te_2; K = 25.1).

Q (vapor, at 1390°) = 281 Cal.

S (vapor) per cubic meter = 0.315 (assumed for Te_2)

per kilo = 0.028 (calc. for Te_2).

Vapor tension, liquid : $\log p = -\frac{9180}{T} + 8.4$ (constants from Trouton's rule, K = 25.1).

at M. P. = 6.3×10^{-5} mm. Hg.

solid : $\log p = -\frac{10,230}{T} + 9.84$.

at 0° C. = 8.1×10^{-32} mm. Hg.

CAESIUM.

Sm (0°—26°) = 0.0482 (Eckhardt and Graefe).

Q (solid, at M. P. = 29°) = 1.4 Cal.

L. H. Fusion = 4.8 Cal. (calculated by 2.1 T rule).

Q (liquid, at M. P.) = 6.2 Cal.

L. H. Vaporization (670°) = 163 Cal. (calculated by Trouton's rule; K = 23).

S (vapor) per cubic meter = 0.225 (assumed).
per kilo = 0.038 (calculated).
Vapor tension, liquid : $\log p = -\frac{4760}{T} + 7.92$ (constants from Trouton's rule; K = 23).
at M. P. = 1.2×10^{-8} mm. Hg.
solid : $\log p = -\frac{4900}{T} + 8.35$.
at 0° C. = 2.5×10^{-10} mm. Hg.

BARIUM.

Sm (0°—100°) = 0.05 (Mendeleeff).
Q (solid, at M. P. = 850°) = 42.5 Cal.
L. H. Fusion = 17.0 Cal. (calculated by 2.1 T rule).
Q (liquid, at M. P.) = 59.5 Cal.

CERIUM.

Sm (0°—100°) = 0.0448 (Hillebrand).
Q (solid, at M. P. = 623°) = 27.9 Cal.
L. H. Fusion = 13.4 Cal. (calculated by 2.1 T rule).
Q (liquid, at M. P.) = 41.3 Cal.
S (liquid) = 0.07 (assumed).

TANTALUM.

Sm. (0°—100°) = 0.0354 (assumed, from at. sp. heat = 6.4).
Sm (0°—t°) = 0.0338+0.000016t (function of t assumed).
Q (solid, at M. P. = 2900°) = 233 Cal.
L. H. Fusion = 37 Cal. (calculated by 2.1 T rule).
Q (liquid, at M. P.) = 270 Cal.

TUNGSTEN.

Sm (0°—t°) (to 423°) = 0.033+0.000011t (Defacqz and Geuchard).
Q (solid at M. P. = 3350°) = 234 Cal.
L. H. Fusion = 40 Cal. (calculated by 2.1 T rule).

Q (liquid, at M. P.) = 274 Cal.
S (liquid) = 0.10 (assumed, same as solid at M. P.).
Q (liquid, at B. $P._{760}$ = 5164°) = 455 Cal.
L. H. Vaporization (5164°) = 743 Cal. (B. P. according to Langmiur).
Q (vapor, at 5164°) = 1198 Cal.
S (vapor) per cubic meter = 0.225 (assumed).
per kilo = 0.027 (calculated).
Vapor tension, liquid : $\log p = -\frac{30{,}000}{T} + 8.4$ (constants from Trouton's rule, K = 25.1).
at M. P. = 1.3 mm. Hg.
solid : $\log p = -\frac{31{,}670}{T} + 8.86$.
at 0° C. = 7.4×10^{-108} mm. Hg.

Osmium.

Sm (19°—98°) = 0.03113 (Regnault).
Sm (0°—t°) = 0.0305+0.000006t (function of t assumed).
Q (solid, at M. P. = 2200°) = 96 Cal.
L. H. Fusion = 36 Cal. (calculated by second rule).
Q (liquid, at M. P.) = 132 Cal.
S (liquid) = 0.057 (assumed from sp. ht. solid at M. P.).
Q (liquid, B. $P._{760}$ = 2600°) = 155 Cal.
L. H. Vaporization (2600°) = 379 Cal. (calculated from Trouton's rule, K = 25.1).
Q (vapor, at 2600°) = 534 Cal.
S (vapor) per cubic meter = 0.225 (assumed).
per kilo = 0.026 (calculated).
Vapor tension, liquid : $\log p = -\frac{15{,}870}{T} + 8.4$ (constants from Trouton's rule; K = 25.1).
at M. P. = 97.7 mm. Hg.
solid : $\log p = -\frac{16{,}880}{T} + 8.81$.
at 0° C. = 9.6×10^{-54} mm. Hg.

IRIDIUM.

Sm (0°—t°) = 0.0317+0.000006t (Violle).
Q (solid, at M. P. = 2360°) = 108 Cal.
L. H. Fusion = 28 Cal. (calculated by second rule).
Q (liquid, at M. P.) = 136 Cal.
S (liquid) = 0.060 (assumed, same as solid at M. P.).
Q (liquid, at B. P_{760} = 2550°) = 147 Cal.
L. H. Vaporization (2550°) = 368 Cal. (calculated from Trouton's rule; K = 25.1).
Q (vapor, at 2550°) = 515 Cal.
S (vapor) per cubic meter = 0.225 (assumed).
per kilo = 0.020 (calculated).
Vapor tension, liquid : $\log p = -\frac{15{,}580}{T} + 8.4$ (constants from Trouton's rule; K = 25.1).
at M. P. = 302 mm. Hg.
solid : $\log p = -\frac{16{,}670}{T} + 8.81$.
at 0° C. = 5.6×10^{-53} mm. Hg.

PLATINUM.

Sm (0°—t°) = 0.0317+0.000006t (Violle).
Q (solid, at M. P. = 1755°) = 75.2 Cal. (Violle).
L. H. Fusion = 27.2 Cal. (Violle).
Q (liquid at M. P.) = 102.4 Cal. (Violle).
S (liquid) = 0.053 (assumed, same as solid at M. P.).
Q (liquid, at B. P_{760} = 2450°) = 139 Cal.
L. H. Vaporization (2450°) = 351 Cal. (calculated from Trouton's rule; K = 25.1).
Q (vapor, at 2450°) = 490 Cal.
S (vapor) per cubic meter = 0.225 (assumed).
per kilo = 0.026 (calculated).
Vapor tension, liquid : $\log p = -\frac{15{,}040}{T} + 8.4$ (constants from Trouton's rule; K = 25.1).
at M. P. = 9.55 mm. Hg.
solid : $\log p = -\frac{16{,}250}{T} + 9.0$.
at 0° C. = 3.0×10^{-51} mm. Hg.

GOLD.

S (0°—600°) = 0.0316 constant (Violle).

Sm (0°—t°)600° to 1064° = $0.0289+0.0000045t+\frac{18.96}{t}$ (Violle).

Q (solid, at M. P. = 1064°) = 34.63 Cal. (from Violle's equation).

L. H. Fusion = 16.30 Cal.

Q (liquid, at M. P.) = 50.93 Cal. (Roberts-Austen).

S (liquid) = 0.0358 (assumed, same as solid at M. P.).

Q (liquid, at B. $P._{760}$ = 2530°) = 103.4 Cal.

L. H. Vaporization (2530°) = 358 Cal. (calculated from Trouton's rule; K = 25.1).

Q (vapor, at 2530°) = 461 Cal.

S (vapor) per cubic meter = 0.225 (assumed).

per kilo = 0.025 (calculated).

Vapor tension, liquid : $\log p = -\frac{15{,}470}{T}+8.4$ (constants from Trouton's rule, K = 25.1).

at M. P. = 6.8×10^{-4} mm. Hg.

solid : $\log p = -\frac{16{,}175}{T}+8.93$.

at 0° C. = 4.8×10^{-51} mm. Hg.

MERCURY.

S (solid) at −59° = 0.0319 (Regnault).

Q (solid) at M.P. −39° = −4.1 Cal.

L. H. Fusion (−39°) = 2.84 Cal. (Person).

Q (liquid, at M. P.) = −1.30 Cal.

Sm (liquid, −36° to 0°) = 0.0333 (Pettersson).

Sm (0°—t°) up to 250° = $0.03337-0.0000027t+0.00000000055t^2$ (Naccari).

Q (liquid, at B. $P._{760}$ = 357°) = 11.7 Cal.

L. H. Vaporization (357°) = 67.8 Cal. (Kurbatoff).

(357°) = 66.8 Cal. } (Calc. thermodynamically, from vapor tension curve).

(0°) = 77.14 Cal. }

L.H.V. at critical temperature (1139°) = 0.0 Cal. } 1139° is calculated critical temperature.

Q (vapor, at 357°) = 79.5 Cal.
(vapor, at 1139° = critical temp.) = 100 Cal.
S (vapor) per cubic meter. = 0.225 (assumed).
per kilo = 0.025 (calculated).
Vapor tension, liquid : $\log p = -\frac{3330.6}{T} + 1.75 \log. T -$ 0.00221T+4.6544 (from vapor tensions at 357°, 260° and 140°).
at M. P. $= 5.13 \times 10^{-6}$ mm. Hg.
solid : $\log p = -\frac{3170}{T} + 8.26$ (8.26 assumed).

THALLIUM.

Sm (17°−100°) = 0.03355 (Regnault).
Sm (0°—t°) = 0.030+0.00002t.
Q (solid, at M. P. = 303°) = 10.9 Cal. (calculated from formula).
L. H. Fusion = 7.2 Cal. (Robertson).
Q (liquid, at M. P.) = 18.1 Cal.
S (liquid) = 0.042 (assumed, from solid at M. P.).
Q (liquid, at B. $P._{760}$ = 1700°) = 77 Cal.
L. H. Vaporization (1700°) = 221 Cal. (calculated by Trouton's rule; K = 23).
Q (vapor, at 1700°) = 298 Cal.
S (vapor) per cubic meter = 0.225 (assumed).
per kilo = 0.025 (calculated).
Vapor tension, liquid : $\log. p = -\frac{9,940}{T} + 7.92$ (constants from Trouton's rule; K = 23).
at M. P. $= 4.7 \times 10^{-10}$ mm. Hg.
solid: $\log p = -\frac{10,260}{T} + 8.5$.
at 0° C. $= 8.3 \times 10^{-30}$ mm. Hg.

LEAD.

Sm (0°—t°) = 0.02925 + 0.000019t (Bede, combined with Regnault).
Q (solid, at M. P. = 327°) = 11.6 Cal. (Le Verrier).
L. H. Fusion = 6.0 Cal. (Richards).
Q (liquid, at M. P.) = 17.6 Cal. (Person).
S (liquid, 335° to 430°) = 0.0402 (Person).

Q (liquid, at B. P.$_{760}$ = 1580°) = 68 Cal.
L. H. Vaporization = 209 Cal. (calculated from vapor tension curve).
Q (vapor, at 1580°) = 277 Cal.
S (vapor) per cubic meter = 0.225 (assumed).
per kilo = 0.024 (calculated).
Vapor tension, liquid: $\log p = -\frac{9500}{T} + 8.0$ calculated from Greenwood's data).
at M. P. = 1.5×10^{-8} mm. Hg.
solid: $\log p = -\frac{9744}{T} + 8.41$.
at 0° C. = 4.9×10^{-28} mm. Hg.

BISMUTH.

Sm (0°—t°) = 0.0285+0.00002t (Bede, combined with Regnault).
Q (solid, at M. P. = 269°) = 9.0 Cal.
L. H. Fusion = 12.0 Cal.
Q (liquid, at M. P.) = 21.0 Cal. (Person).
Sm (liquid, 280° to 360°) = 0.0363 (Person).
Q (liquid, at B. P.$_{760}$ = 1435°) = 63 Cal.
L. H. Vaporization (1435°) = 208 Cal. (calculated from vapor tension curve).
Q (vapor, at 1435°) = 271 Cal.
S (vapor) per cubic meter = 0.225 (assumed).
per kilo = 0.024 (calculated).
Vapor tension, liquid: $\log p = -\frac{9460}{T} + 7.45$ (from experimental data).
at M. P. = 1×10^{-10} mm. Hg.
solid: $\log p = -\frac{10{,}000}{T} + 8.45$.
at 0° C. = 6.6×10^{-29} mm. Hg.

RADIUM.

Sm 0° = 0.027 (from Dulong and Petit's Law).
Sm (0°—t°) = 0.027+0.000015t (coefficient of t assumed).
Q (solid, at M. P. = 700°) = 26.3 Cal.
L. H. Fusion = 9.0 Cal. (calculated by 2.1 T rule).

Q (liquid, at M.P.) = 35.3 Cal.
S (liquid) = 0.048 (assumed, same as solid at M. P.).
S (vapor) per cubic meter = 0.225 (assumed).
per kilo = 0.022 (calculated).

THORIUM.

Sm (0°−100°) = 0.0276 (Nilson).
Sm (0°−t°) = 0.0270+0.000008t (coefficient of t assumed).
Q (solid, at M. P. = 1690°) = 68.5 Cal.
L. H. Fusion = 18.0 Cal. (calculated by 2.1 T rule).
Q (liquid, at M. P.) = 86.5 Cal.
S (liquid) = 0.054 (assumed, same as solid at M. P.).
S (vapor) per cubic meter = 0.225 (assumed)
per kilo = 0.022 (calculated).

URANIUM.

Sm (0°−98°) = 0.028 (Blümcke).
Sm (0°−t°) = 0.0275+0.000007t (coefficient of t assumed).
Q (solid, at M. P. = 2000°) = 83 Cal.
L. H. Fusion = 20 Cal. (calculated by 2.1 T rule).
Q (liquid, at M. P.) = 103 Cal.
S (liquid) = 0.055 (assumed, same as solid at M. P.).
Q (liquid, at B. $P._{760}$ = 2900°) = 152 Cal.
L. H. Vaporization (2900°) = 333 Cal. (calculated from Trouton's rule; K = 25.1).
Q (vapor, at 2900°) = 485 Cal.
S (vapor) per cubic meter = 0.225 (assumed).
per kilo = 0.021 (calculated).

Vapor tension, liquid : $\log p = -\frac{17{,}400}{T} + 8.4$ (constants from Trouton's rule; K = 25.1).

at M. P. = 5.5×10^{-6} mm. Hg.

solid : $\log p = -\frac{17{,}975}{T} + 8.85$

at 0° = 1×10^{-57} mm. Hg.

In several of the preceding instalments we have given the heats of formation of alloys and compounds and the thermophysics of the elements. Before passing to the thermophysics of alloys and compounds and problems involving their use, we will consider a few simple cases of the application of data so far given. Such include operations in which metals are melted or volatilized, or amalgams retorted. A few words may be in order, to clear the ground, regarding what is to be regarded as the efficiency of a furnace.

Efficiency of Furnaces.

Under this term we must distinguish a generic sense and a specific sense, the first referring to furnaces in which the object is to maintain a certain temperature for a certain time with the minimum consumption of fuel, the second, in which the object is to perform a certain thermal operation with the smallest consumption of fuel. In the first case, one furnace may be compared with another, and thus comparative efficiencies calculated; in the second case real or absolute efficiencies can be also calculated. A few examples will illustrate this difference, which is an essential difference as far as making calculations is concerned.

Cases of Specific Efficiency: Whenever it is desired to melt a metal for the purpose of casting it, a certain definite amount of heat must be imparted to the metal, and the ratio between this efficiently utilized heat and the heating power of the fuel consumed, is the efficiency of the furnace. If the furnace is electric the theoretical heat value of the electric energy used is the divisor. If, in addition to the heat required to raise the substances to the desired temperature, there is also heat absorbed in chemical reactions, this amount can be added in as usefully applied heat, and the sum of this and the heat in the final products be regarded as the total efficiently applied heat. If a blast furnace takes iron ore and furnishes us melted pig iron, the sum of the heat absorbed in the chemical decomposition of the iron oxide and the sensible heat in the melted pig iron is the efficiently applied heat, because it is the necessary theoretical minimum required; all other items are more

or less susceptible of reduction, but these are necessary items and, therefore, measure the net efficiency. If my dwelling requires 200 cubic feet of hot air per minute at 150° F. to keep it at 65° F., while the outside air is at 0° F., the ratio of the heat required to warm the 200 cubic feet of air from 0° F. to 150° F., to the calorific power of the fuel used per minute, measures the *specific* efficiency of the "heater;" the question whether this amount of hot air keeps the temperature of the rooms at 65° F. is a question of the *general* efficiency of the construction of the house.

Cases of Generic Efficiency: Such are those in which practically all the heat generated eventually leaves the furnace by radiation or conduction, or useless heat in waste gases; this is the case when a certain temperature has to be continuously maintained for a given time, and where the *time* element is the controlling one, and not any definite amount of thermal work is to be done. Examples are numerous: An annealing furnace, where steel castings, let us say, are to be kept at a red heat for two days, or a brick kiln, where several days slow burning are required, or a puddling furnace, where the melted iron must be held one to two hours to oxidize its impurities. In all these cases we may say that one furnace keeps its contents at the right heat for the right time with so much fuel, another does the same work with 10 or 25 per cent. less fuel, and is, therefore, 10 or 25 per cent. more efficient; but we cannot, in the nature of the case, speak of the absolute or specific efficiency of the furnace, because there is no definite term, expressible in calories, to compare with the thermal power of the fuel.

In many cases the two efficiencies are mixed in the same process or operation, and then the calculation of absolute or specific efficiency can be made for that portion of the operation wherein a certain definite amount of thermal work is done. Thus, in an annealing kiln, 50 tons of castings may be brought up to annealing heat in 24 hours, starting cold, and the heat absorbed by the castings compared with the calorific power of the coal burnt during this period, is a measure of the real efficiency of this part of the operation. During the rest of the operation, while the castings are simply kept at annealing heat,

there can be no calculation of the absolute or specific efficiency of the furnace, because one of the terms necessary for the comparison has disappeared, in that part of the process we can only speak of relative efficiency compared to some other furnace doing a similar operation.

It goes, almost without saying, that we can, of course, apply the conception of efficiency in its relative or general sense to the whole operation or to any part of it

Problem 6.

The Rockwell Engineering Co. state in their current advertisements that their regenerative oil-burning furnace melts 100 pounds of copper with the consumption of less than 1.5 gallons of oil. Assume that 1.5 gallons of oil is used, and that the copper is heated from 25° C. to melted metal 100° C. above its melting point.

Required: The "efficiency" of the furnace; *i.e.*, its specific efficiency as calculated from the net heat utilized.

Solution: One gallon of fuel oil averages in weight 7.5 pounds, and its calorific power 11,000 Calories per kilogram, or 11,000 pound Calories per pound. The calorific power of the fuel used in melting 100 pounds of copper is therefore:

Heat generated $11{,}000 \times 7.5 \times 1.5 = 82{,}500 \times 1.5 = 123{,}750$ pound Calories.

The heat imparted to the copper is as follows, taking the data from Article V. of these calculations: (p. 68.)

Heat in 1 lb. melted copper at melting point	=	162 lb. Cal.
Heat in 1 lb. solid copper at 25° C.	=	2 "
Heat required to just melt the copper	=	160 "
Heat to superheat liquid copper 100° C. 0.133×100	=	13 "
Total heat expended on each pound of copper	=	173 "
Heat usefully applied per 100 pounds	=	17,300 "

$$\text{Net efficiency of furnace} = \frac{17{,}300}{123{,}750} = 0.14 = 14\%$$

It is proper to remark that although this efficiency appears low, yet it is considerably greater than is attained in simple melting holes or wind furnaces, and yet the calculations show

what a large margin for improvement and greater efficiency exists in even some of the best and relatively most efficient metallurgical furnaces.

Problem 7.

In the distillation of silver amalgam in iron retorts, 1000 kilos, of amalgam, containing 200 kilos. of silver, is retorted with the consumption of 550 kilos. of wood, the mercury vapor passes off at an average temperature of 450° C., and the silver is raised towards the end of the operation to 800° C., in order to expel the last of the mercury. Assume the calorific power of the wood 3000 Calories.

Required: The net efficiency of the furnace.

Solution: The heating power of the wood is $550 \times 3000 =$ 1,650,000 Calories.

The heat utilized is that absorbed in separating the silver from the mercury plus the sensible heat in the mercury vapor at 450°, plus the sensible heat in the silver at 800°. These are calculated as follows:

Heat to decompose amalgam = 2470 Calories per 108 kilos. of silver $= 200 \times (2470 \div 108) = 200 \times 22.9 =$ **4,580** Calories.

Heat in silver at 800°, using Pionchon's formula, is 800 $[0.05758 + 0.0000044\ (800) + 0.000000006\ (800)^2] \times 200 =$ 10,390 Calories.

Heat in 800 kilos. of mercury vapor at 450° is

(*a*) heat to boiling point (**Naccari**) 357 $[0.03337 - 0.00000275\ (357) + 0.0000000667\ (357)^2] \times 800$	=	11,677 Cal.
(*b*) heat to vaporize 72.5×800	=	58,000 "
(*c*) heat in vapor at 450° = $0.025 \times (450 - 357) \times 800$	=	1,880 "
Total	=	71,557 "

Heat usefully applied:

In decomposing amalgam	=	4,580 "
In mercury vapor, as sensible heat	=	71,557 "
In silver, as sensible heat	=	10,390 "
Total	=	86,527 "

$$\text{Efficiency of furnace} = \frac{86,527}{1,650,000} = 0.052 = 5.2\%.$$

Problem 8.

In a zinc works, impure zinc is refined by redistillation in fire-clay retorts, a bank of retorts distilled 970 kilos. of zinc with the expenditure of 912 kilos. of small anthracite coal. Assume that the zinc vapors pass out of the muffles at the boiling point (930°).

Required: (1) The net efficiency of the furnace.

(2) The electrical power which would be required, in horse-power-hours, to do the same work, assuming the heating efficiency of the electric furnace is 75 per cent.

Solution: (1) The small anthracite may be assumed to have a calorific power of 7850 Calories; therefore, the total heat which should be developed is $7850 \times 912 = 7{,}159{,}200$ Calories. The heat in 1 kilo. of zinc in the state of vapor at its boiling point can be calculated from the thermophysical data supplied for zinc as:

(*a*) In solid zinc to melting point (420°)	45.20	Cal.
(*b*) Latent heat of fusion	22.61	"
(*c*) Heat in melted zinc to boiling point (930°)	65.05	"
(*d*) Latent heat of vaporization	425.00	"
Total	557.86	"

Heat required for 970 kilos. = 541,124 "

$$\text{Efficiency of furnace} = \frac{541{,}124}{7{,}159{,}200} = 0.075 = 7.5\%.$$

(2) One electric horse-power-hour = 644.0 Cal.
Efficiently applied heat = $644 \times .75$ = 483.0 "

$$\text{Electric horse-power-hours required} = \frac{489{,}995}{483} = 1013 \text{ E.H.P hours}$$

$$\text{One metric ton of zinc requires } \frac{1013}{0.970} = 1044 \text{ E.H.P. hours.}$$

$$\text{Cost of power, at \$20.00 per E. H. P. year} = \frac{20.00}{8766} \times 1044 =$$

$0.00228 \times 1044 = \$2.38$.

This cost of electric power would replace the use of $\frac{0.912}{0.970}$ metric tons of small anthracite, equal to a cost of $2.53 for

electric power sufficient to replace a metric ton of coal for this purpose.

Many other examples could be given of the technical use of the thermophysical data concerning the elements, but the problems given illustrate the methods of calculation.

When one is acquainted with some of the ordinary metallurgical operations, such as melting and distilling the metals, it is surprising to notice how little is known or thought of the efficiency or lack of efficiency of the furnaces used. One man melts 100 pounds of metal by the use of 150 pounds of coal, he builds a new furnace and does it more cheaply by using 100 pounds of coke, which is certainly relatively more efficient; but it is seldom that the operator knows that in one case he is getting probably only 7 per cent. efficiency from his fuel and in the other case only 10 per cent. It is the knowledge of these absolute efficiencies which tells the practical man just what he is accomplishing, and shows him how much room there still remains for improvement.

Thermophysics of Alloys.

There does not exist, in technical literature, much data of this nature concerning alloys. There is here a wide and interesting field for metallurgical research, whose cultivation would yield results both of high practical and high theoretical interest, and yet it is comparatively untouched. What is wanted is complete data concerning the specific heat of solid and liquid alloy, and latent heat of fusion. These, combined with the determination of the heat evolved in the alloying, would furnish a sound basis for a practical theory of alloys, besides enabling workers with these alloys to control the efficiency of their furnaces and, in general, to know with scientific exactness what they are accomplishing.

Alloys of Tin and Lead.

Per Cent. of Tin.	Sm.	Latent Heat of Fusion.
4.8 ($Pb^{16}Sn$)	.....	5.5 (Mazotto)
10.2 ($Pb^{5}Sn$)	.....	8.0 at 307° (Spring)
12.5 ($Pb^{4}Sn$)	.....	8.3 at 292° (Spring)

Per Cent. of Tin.	Sm.	Latent Heat of Fusion.
16.0 (Pb^3Sn)	.....	9.1 at 289° (Spring)
22.2 (Pb^2Sn)	.....	9.5 at 270° (Spring)
		7.9 (Mazotto)
36.3 (PbSn)	0.04073 (12°—99°) (Regnault)	11.6 at 241° (Spring)
		9.4 (Mazotto)
50.0 = total heat to 0° in 1 kilo. melted metal		18.0 from 202° (Ledebur)
53.3 ($PbSn^2$)	0.04507 (10°—99°) (Regnault)	10.5 at 197° (Mazotto)
63.1 ($PbSn^3$)	.....	15.5 at 179° (Spring)
69.5 ($PbSn^4$)	.....	17.0 at 188° (Spring)
83.0 = total heat to 0° in 1 kilo. melted metal		21.5 from 205° (Ledebur)
90.1 ($PbSn^{10}$)	.....	12.9 (Mazotto)

Alloys of Tin and Bismuth.

Per Cent. of Tin.	Sm.	Latent Heat of Fusion.
6.7 (Bi^8Sn)	.....	11.4 Cal. (Mazotto)
22.1 (Bi^2Sn)	.....	11.2 Cal. (Mazotto)
36.2 (BiSn)	0.0400 (20°—99°) (Regnault)	11.6 Cal. (Mazotto)
53.1 ($BiSn^2$)	solid, 0.0450 (Regnault) liquid, 0.0454 (146°—275°) Person	11.6 (Cal. Mazotto)
69.1 ($BiSn^4$)	.....	11.1 Cal. at 140° (Mazotto)
82.7 ($BiSn^8$)	.....	12.6 Cal. (Mazotto)
90.1 ($BiSn^{16}$)	.....	12.8 Cal. (Mazotto)

Alloys of Tin and Zinc.

Per Cent. of Tin.	Sm.	Latent Heat of Fusion.
78.4 ($ZnSn^2$)	.....	23.5 Cal. (Mazotto)
92.7 ($ZnSn^7$)	.....	16.2 Cal. at 197° (Mazotto)
95.6 ($ZnSn^{12}$)	.....	16.3 Cal. (Mazotto)
97.3 ($ZnSn^{20}$)	.....	15.1 Cal. (Mazotto)

Alloys of Tin and Copper.

Bell metal (20 per cent. tin) Sm (14°—98°) = 0.0862 (Regnault).

Bronze (15 per cent. tin).

Total heat in melted metal (to 0°) = 130 Cal. (Ledebur).

If strongly superheated = 143.5 Cal. (Ledebur).

Alloys of Tin and Antimony.

Britannia metal (90 per cent. tin) requires to melt it, starting cold, 28.0 Calories per kilogram (melting point 236°); with 82 per cent. of tin, 25.7 Calories; melting point 205° (Ledebur).

Alloys of Tin, Bismuth and Antimony.

$BiSn^2Sb$ (bismuth 34.3, tin 41.9, antimony 23.8 per cent.).

Sm (15°—100°) = 0.0462 (Regnault).

Alloy of Tin, Bismuth, Antimony and Zinc.

$BiSn^2SbZn^2$ (bismuth 29.8, tin 34.0, antimony 17.3, zinc 18.9 per cent.).

Sm (15°—100°) = 0.0566 (Regnault).

Alloys of Lead and Bismuth.

Per Cent. of Lead.	Sm.	Latent Heat of Fusion.
11.1 ($PbBi^8$)	.....	10.2 (Mazotto)
33.2 ($PbBi^2$)	.....	6.4 (Mazotto)
39.9 (Pb^2Bi^3)	solid, 0.03165 (16°—99°) Person. liquid, 0.03500 (144°—358°) Person	
42.7 (Pb^3Bi^4)	.....	4.7 at 127° (Mazotto)
49.9 (PbBi)	.....	4.0 (Mazotto)
66.6 (Pb^2Bi)	.....	3.6 (Mazotto)
88.8 (Pb^8Bi)	.....	4.9 (Mazotto)

Alloys of Lead and Antimony.

With 63.0 per cent of lead, Sm (10°—98°) = 0.0388 (Regnault)

With 82.0 per cent. of lead, heat in 1 kilo. melted metal = 15.6 Calories (Ledebur).

With 90.0 per cent. of lead, total heat in 1 kilo. melted metal = 13.8 Calories (Ledebur).

Alloys of Lead, Tin and Bismuth.

D'Arcet's Alloy, containing 32.5 lead, 18.5 tin, 48.7 bismuth

Sm solid (5°—65°)	= 0.0372 (Mazotto)
Sm solid (12°—50°)	= 0.049 (Person).
Sm solid (14°—80°)	= 0.060 (Person).
Sm liquid (107°—136°)	= 0.047 (Person).
Sm liquid (120°—150°)	= 0.0399 (Mazotto).
Sm liquid (136°—300°)	= 0.0360 (Person).
Latent heat of fusion	= 5.96 Cal. at 96° (Person).
	= 5.77 Cal. at 99° (Mazotto).

Rose's Alloy, containing 24.0 lead, 27.3 tin, 48.7 bismuth:

Sm solid (5°—65°)	= 0.375 (Mazotto).
Sm fluid (119°—338°)	= 0.0422 (Person).
Latent heat of fusion	= 6.85 Cal. at 99° (Mazotto).

Fusible Alloy, containing 31.8 lead, 36.2 tin, 32.0 bismuth:

Sm solid (18°—52°)	= 0.0423 (Person).
Sm solid (11°—98°)	= 0.0448 (Regnault).
Sm fluid (143°—330°)	= 0.0460 (Person).
Latent heat of fusion	= 7.63 Cal. at 145° (Person).

Wood's Alloy, containing 25.8 lead, 14.7 tin, 52.4 bismuth: 7 cadmium:

Sm solid (5°—50°)	= 0.0352 (Mazotto).
Sm fluid (100°—150°)	= 0.0426 (Mazotto).
Latent heat of fusion	= 7.78 Cal. at 75° (Mazotto).

Lipowitz's Alloy, containing 25.0 lead, 14.2 tin, 50.7 bismuth, 10.1 cadmium:

Sm solid (5°—50°)	= 0.0345 (Mazotto).
Sm fluid (100°—150°)	= 0.0426 (Mazotto).
Latent heat of fusion	= 8.40 Cal. at 75° (Mazotto).

Alloys of Copper and Zinc.

Red Brass	S at 0°	= 0.0899 (Lorenz)
	S at 50°	= 0.0924 (Lorenz)
(Copper 85%)	S at 75°	= 0.0940 (Lorenz)
Yellow Brass	S at 0°	= 0.0883 (Lorenz)
	at 50°	= 0.0922 (Lorenz)
(Copper 65%)	at 175°	= 0.0927 (Lorenz)

Heat in 1 kilo. of melted, somewhat superheated, brass = 130 Calories (Ledebur).

Alloys of Copper, Zinc and Nickel.

German Silver:

(74Cu. 20Zn. 6Ni) Sm(0—t) = 0.0941 + 0.0000053t (Tomlinson)

Alloys of Copper and Aluminium.

Copper 88.7% Sm (20°—100°) = 0.10432 (Luginin)

Alloys of Silver and Platinum.

Silver 66.7% Sm (0—t) = 0.04726 + 0.0000138t (Tomlinson).

Alloys of Mercury and Tin.

HgSn (37.1% Sn) Sm (—30°—15°) = 0.04083 (Schüz)
(—25°—15°) = 0.04218 (Schüz)
(22°—99°) = 0.07294 (Regnault)
HgSn (54.1% Sn) Sm (25°—99°) = 0.06591 (Regnault)
$HgSn^5$(74.7% Sn) Sm (—16°—15°) = 0.05039 (Schüz)

Alloys of Mercury and Lead.

Pb Hg (50.9% Pb) Sm (—69°—20°) = 0.03458 (Schüz)
Sm (23°—99°) = 0.03827 (Regnault)
Pb^2Hg (67.4% Pb) Sm (—72°—20°) = 0.03348 (Schüz)

Alloys of Cadmium and Tin.

$CdSn^2$ (67.8% Sn) Sm (—77°—20°) = 0.05537 (Schuz)
whence we have Sm (0 — t) = 0.0557 + 0.00000366t (Schüz)

Alloys of Iron and Carbon.

Soft Steel (0.15% carbon) Sm (20°—98°) = 0.1165 (Regnault).
Hard Steel (1.00% carbon) Sm (20°—98°) = 0.1175 (Regnault).
Total heat in 1 kilo melted steel at 1350° = 300 Calories (Ledebur).

Cast Iron (4.0% carbon) Sm (0—1200°) = 0.175.
Sm (0—t°) = 0.12 + 0.000046t
Total heat in 1 kilo. melted at 1200° = 245 Calories (Ledebur).
Total heat in 1 kilo. coming from blast furnace = 250 to 325 Calories (Akermann).

Problem 9.

A steel-melting crucible contains 110 pounds of steel, which is melted in a wind furnace with the use of 150 pounds of coke. Assume the coke to be 90 per cent. fixed carbon, and the steel to be superheated 100° C. above its melting point.

Required: The net efficiency of the furnace.

Solution: The calorific power of the coke may be assumed as 90 per cent. that of pure carbon, and therefore:

$= 150 \times (8100 \times 0.90) = 150 \times 7290 = 1{,}093{,}500$ lb. Cal.

Heat in steel at melting point:

110×300 (Ledebur) $= 33{,}000$

Heat to superheat 100°:

$110 \times 100 \times 0.15$ (assumed) $= 1{,}650$

Total $34{,}650$ lb. Cal.

$$\text{Efficiency of furnace} = \frac{34{,}650}{1{,}093{,}500} = 0.032 = 3.2\%$$

Problem 10.

A Siemen's regenerative furnace holds eighteen steel crucibles, each containing 100 pounds of steel. Assume that the efficiency of utilization of the heat for melting the steel is 5 per cent., and that the furnace is fed by natural gas, having a calorific power of 512-pound Calories per cubic foot.

Required: The number of cubic feet of natural gas required per furnace heat of eighteen crucibles = 1800 pounds of cast steel.

Solution: Heat in steel $= 1800 \times 315 = 567{,}000$ lb. Cal.

$$\text{Heating power of gas required} = \frac{567{,}000}{0.05} = 11{,}340{,}000 \text{ lb. Cal.}$$

$$\text{Cubic feet of gas required} = \frac{11{,}340{,}000}{512} = 22{,}150 \text{ cubic feet.}$$

Gas required per ton of steel, 2000 lbs. = 24,610 cubic feet.

Cost of gas, at \$0.08 per 1000 cubic feet = \$1.97.

Problem 11.

In a malleable-casting foundry the pig iron is melted in a reverbatory air furnace, 3000 kilos. being melted in two hours

by the combustion of 1200 kilos. of bituminous coal, having a calorific power of 8500 Calories.

Required: The melting efficiency of the furnace.

Solution: Calorific power of coal used:

$$1200 \times 8500 = 10{,}200{,}000 \text{ Calories.}$$

Heat in melted iron at foundry heat:

$$3000 \times 250 \text{ (Ledebur)} = 750{,}000 \text{ Calories.}$$

$$\text{Efficiency of furnace} = \frac{750{,}000}{10{,}200{,}000} = 0.0735 = 7.35\%$$

Problem 12.

In an iron foundry cupola 14 metric tons of pig iron are melted in one hour, using 1.5 tons of coke (90 per cent. carbon). The gases passing away contain by volume CO 13 per cent., CO^2 13 per cent., nitrogen 74 per cent., and leave the cupola at 500° C. The body of the cupola is 1.5 meters in diameter outside and 4 meters high.

Required:

(1) The net melting efficiency of the cupola.

(2) The proportion of the calorific power of the coke lost.

(*a*) By the sensible heat of the hot gases escaping.

(*b*) By the imperfect combustion of the coke.

(*c*) By radiation from bottom and walls of the cupola.

(3) The amount of heat in Calories radiated, on an average, from each square meter of outside surface per minute.

Solution:

(1) Calorific power of the coke;

$$1500 \times 0.90 \times 8100. = 10{,}935{,}000 \text{ Calories.}$$

Heat in melted iron:

$$14{,}000 \times 250 \text{ (Ledebur)} = 3{,}500{,}000 \text{ Calories.}$$

$$\text{Efficiency of melting} = \frac{3{,}500{,}000}{10{,}935{,}000} = 0.32 = 32\%$$

(2 *a*) Weight of carbon escaping $= 1500 \times 0.90 = 1350$ kilos.

Volume of CO and CO^2 escaping $= \frac{1350}{0.54} = 2500\ m^3$

(Because 1 m^3 of either gas carries 0.54 kilos. C.)

Volume of escaping gas $= \frac{2500}{0.13+0.13} = 9615\ m^3$

Volume of nitrogen (by difference) $= 7115\ m^3$

Sensible heat of nitrogen and CO

$(7115+1250)\times[0.303\ (500)+0.000027\ (500)^2] = 1,323,760$ Cal.

Sensible heat of CO^2

$1250\times[0.37\ (500)+0.00022\ (500)^2] = 300,000$ "

Total sensible heat in gases $= 1,623,760$ "

Proportion of calorific power of the fuel thus lost:

$$= \frac{1,623,760}{10,935,000} = 0.1485 = 14.85\%.$$

(2, *b*) Volume of CO escaping $= 1250\ m^3$

Calorific power of this gas $= 1250\times 3062 = 3,827,500$ Cal.

Proportion of calorific power of the fuel thus lost:

$$= \frac{3,827,500}{10,935,000} = 0.35 = 35\%$$

(2, *c*)

Heat in pig iron	=	3,500,000 Cal.
Heat in waste gases	=	1,623,760 "
Lost by imperfect combustion	=	3,827,500 "
Accounted for		8,951,260 "
Calorific power of the coke	=	10,935,000 "
Difference, loss by radiation	=	1,983,740 "

Proportion of calorific power of the fuel thus lost:

$$= \frac{1,983,740}{10,935,000} = 0.1815 = 18.15\%$$

(3)

Area of bottom of cupola $= (1.5)^2\times 0.7854$	=	1.77 m^2
Area of sides of cupola $= 1.5\times 3,14\times 4$	=	18.85 m^2
Total radiating area	=	20.62 m^2

Heat radiated per sq. m. per hour $= \frac{1,983,740}{20.62} = 96,200$ Cal.

Heat radiated per sq. m. per min. $= \frac{96,200}{60} = 1,603$ "

In general, we may state that the net efficiency in melting, etc., of metals is very various, from, say, 2 or 3 per cent. in a crucible steel-melting wind furnace to about 10 or 15 per cent. in reverberatory furnaces, 20 to 30. per cent in regenerative open-hearth furnaces, 30 to 50 per cent. in shaft furnaces, where material to be heated and fuel burned are in direct contact with each other, 50 to 75 per cent. in steam boilers and hot-blast stoves, and 60 to 85 per cent. in large electrical furnaces.

CHAPTER V.

THERMOPHYSICS OF CHEMICAL COMPOUNDS.

The metallic oxides are the most important compounds occurring in metallurgy, together with the oxides of hydrogen, carbon and of sulphur, arsenic and antimony, which are formed during combustion and in roasting operations. We do not include as oxides those combinations of two or more oxides in chemical proportions, such as of silica with metallic oxides, which form oxygen salts or ternary oxygen compounds. They will be separately discussed. In the following lists Sm, as before, means the mean specific heat per kilogram, in large Calories (or per pound in lb. Cal.) in the range of temperature given; S means actual specific heat at the temperature given, and Q is the quantity of heat absorbed in fusion or volatilization or in passing through any designated range of temperature. Temperatures are given only in centigrade degrees, excepting that t signifies Fahrenheit temperature; volumes of gases are understood as being at 0° C. and 760 m.m. pressure, unless distinctly stated otherwise.

Oxides.

Hydrogen Oxide, H^2O:

Ice	Sm (—78°—0°)	= 0.463 (Regnault).
	(—30°—0°)	= 0.505 (Person).
Water—	Sm (0°—100°)	= 1+0.00015t (Pfaundler).
	S (at 15°)	= 1.0045 (Pfaundler).
	S (at 0°)	= 1.0000 (assumed).

In all metallurgical calculations it will be sufficiently exact to assume the specific heat of water at ordinary temperatures as unity. In heating to the boiling point, from zero, 101.5 Calories are absorbed.

Gas Sm (0° to t°)

1 m^3 up to 2000°	= 0.34+0.00015t (Mallard and Le Chatelier).
1 m^3 2000°—4000°	= 0.48+0.00017t (Vielle).
1 ft^3 up to 2000°	= 0.021+0.000009t—lb. Cal.
1 ft^3 2000°—4000°	= 0.030+0.000011t—lb. Cal.
1 kilo. up to 2000°	= 0.42+0.000185t—Cal.
1 kilo. 2000°—4000°	= 0.59+0.00021t Cal.
1 lb. up to 2000°	= 0.42+0.000185t—lb. Cal.
1 lb. 2000°—4000°	= 0.59+0.00021t—lb. Cal.
1 ft^3 up to 3600° F.	= 0.021+0.000005t B. T. U.
1 ft^3 3600°—7200° F.	= 0.030+0.000006t B. T. U.
1 lb. up to 3600° F.	= 0.42+0.000103t B. T. U.
1 lb. 3600°—7200° F.	= 0.59+0.00012t B. T. U.

Above figures are for water vapor as it exists in almost all metallurgical problems, as true gas far removed from its maximum tension at any given temperature. When the water vapor exists as saturated steam under its maximum tension, as in a steam boiler, it is recommended to consult tables giving the total heat in steam at any temperature condensing to liquid water at 0°, or to use Regnault's formula for the same:

$$Q = 606.5+0.305t$$

which expresses the amount of heat required to convert 1 kilogram of water, liquid at 0°, into steam at its maximum pressure at the temperature t. A little reflection will show that the above formula amounts to taking the specific heat of a kilogram of saturated steam, under a constantly *increasingpressure*,

as	$Q = 0.305t$
or under increasing pressure	$Sm = 0.305$
or per cubic meter (0.81 kilos.)	$Sm = 0.247$

These figures apply to boiler practice only. In cases where water is evaporated at or below 100° C., and converted afterwards into steam at a high temperature, I recommend first calculating the heat required to convert the water into vapor at 0° (606.5 Cal.) and then treating the vapor afterwards as true gas, by the formulæ of Mallard and Le Chatelier. This puts water vapor at once, from the beginning, on the same footing as all the other gases, and greatly simplifies all subsequent calculations, without introducing any unnecessary errors.

Latent heat of fusion = 80 Cal. (Bunsen).
Latent heat of vaporization = 606.5 Cal. at 0° (Regnault).
= 600.0 Cal. at 10°.
= 537.0 Cal. at 100° (to vapor at 760 m m).
Total heat in saturated steam = 606.5 + 0.305t (Regnault).

Most metallurgical problems which have to do with converting moisture in fuel, ores, etc., into vapor, are concerned with the evaporation of the water far below 100° by means of dry gases, into which the water vapor enters at a partial pressure, which is only a small fraction of atmospheric pressure. The problem is, in these cases, to find how much heat is necessary to convert the water into vapor at the low temperature corresponding to such low pressure. By finding the temperature corresponding to said partial pressure, as a maximum tension, applying Regnault's formula, we get the heat absorbed in producing the vapor at that temperature. We can then add to this the heat required to raise the vapor up to the higher temperature at constant pressure, using Mallard and Le Chatelier's formulæ.

Example: Wet peat is dried in a kiln by hot air, the issuing air being at 50° C. and the tension of the moisture in it 25 millimeters. How much heat is absorbed in latent heat, and how much as sensible heat per 1 kilogram of water evaporated?

Solution: The tension, 25 millimeters, is the maximum tension of aqueous vapor at 26° (Tables). To change 1 kilogram of water at zero to saturated vapor at 26° requires, according to Regnault's formula, 606.5 + 0.305 (26) = 614 Calories. (The real latent heat of vaporization at 26° is, therefore, 614—26 = 588 Calories.) The heat required to evaporate 1 kilogram of water under the conditions of the peat kiln is therefore:

Heat to produce vapor at 25 m.m. (26°) = 614.0 Calories.
Heat to raise vapor from 26° to 50° (constant pressure) = $[0.42 + 0.000185\ (50 + 26)] \times (50 - 26)$ = 10.4 "
Total = 624.4 "

In most cases of drying or evaporation the results will be sufficiently accurate by assuming the water first evaporated at

0°, with latent heat of evaporation 606.5 Calories, and then raised as gas to the end temperature. The difference between this method and the above will be small, where the temperature of the issuing gas is below 100° and the proportion of vapor in it small; where the temperature of issuing gas is high and the amount of vapor in it large, the more exact method should be used. To facilitate this, the maximum tension of aqueous vapor for temperatures up to 100° is here given:

Temperature C°.	Max. Tension. mm. of Hg.	Temperature C°.	Max. Tension. mm. of Hg.
0°	4.6	50°	92.0
5°	6.5	55°	117.5
10°	9.1	60°	148.9
15°	12.7	65°	187.1
20°	17.4	70°	233.3
25°	23.5	75°	288.8
30°	31.5	80°	354.9
35°	41.8	85°	433.2
40°	54.9	90°	525.5
45°	71.4	95°	633.7
50°	92.0	100°	760.0

Beryllium Oxide, Be^2O^3

Sm (0°—100°) = 0.2471 (Nilson and Pettersson).

Boric Oxide, B^2O^3:

Sm (16°—98°) = 0.2374 (Regnault).

Carbonous Oxide, CO:

Sm (0° to t°) 1 m^3 up to 2000° = 0.303 + 0.000027t (Mallard and Le Chatelier).

1 m^3 2000°—4000° = 0.2575 + 0.000072t (Berthelot).

1 ft^3 up to 2000° = 0.0189 + 0.0000017t lb. Cal.

1 ft^3 2000°—4000° = 0.0161 + 0.0000045t lb. Cal.

1 kilo. up to 2000° = 0.2405 + 0.0000214t Cal.

1 kilo. 2000°—4000° = 0.2044 + 0.000057t Cal.

1 lb. up to 2000° = 0.2405 + 0.0000214t lb. Cal.

1 lb. 2000°—4000° = 0.2044 + 0.000057t lb. Cal.

1 $ft.^3$ up to 3600° F. = 0.0189 + 0.0000009*t* B. T. U.

1 ft. 3600—7200° F. = 0.0161 + 0.0000025*t* B. T. U.

1 lb. up to 3600° F. = 0.2405 + 0.0000119*t* B. T. U.

1 lb. 3600°—7200° F. = 0.2044 + 0.000032*t* B. T. U.

Carbonic Oxide, CO^2:

There has been much doubt about the specific heat of this gas, and several experimenters have given it particular attention. Direct combustion of CO to CO^2 in air has recently given Mallard and Le Chatelier a directly-observed temperature of 2050°, while the formula, which has so far been considered by us as the most reliable (Sm = 0.37 + 0.00027t), leads to 1947°. After renewed consideration of the whole subject the writer considers the best values those given below, because by accepting these they will agree with the observed temperature of combustion, 2050°. We will hereafter use these values instead of the one just above. Above 2000° the values of Berthelot and Vielle are the only ones to be used.

Sm (0° to t°) 1 m^3 up to

2050°	= 0.37 + 0.00022t (calculated by Richards).
1 m^3 2000°—4000°	= 0.815 + 0.0000675t (Vielle).
1 ft^3 up to 2050°	= 0.023 + 0.000014t lb. Cal.
1 ft^3 2000°—4000°	= 0.051 + 0.0000042t lb. Cal.
1 kilo. up to 2050°	= 0.19 + 0.00011t Cal.
1 kilo. 2000°—4000°	= 0.42 + 0.000034t Cal.
1 lb. up to 2050°	= 0.19 + 0.00011t lb. Cal.
1 lb. 2000°—4000°	= 0.41 + 0.000034t lb. Cal.
1 ft^3 up to 3700° F.	= 0.023 + 0.000008*t* B. T. U.
1 ft^3 36000 —7200° F.	= 0.051 + 0.0000023*t* B. T. U.
1 lb. up to 3700° F.	= 0.19 + 0.00006*t* B. T. U.
1 lb. 3600°—7200° F.	= 0.41 + 0.000019*t* B. T. U.

In all the above formulæ, Q from t° to 0° is equal to Sm multiplied by t; *e.g.*, Q (0° to t°) 1 m^3 to 2050° = $0.37t + 0.00022t^2$.

Nitrogen Peroxide, NO^2:

Sm (27°—280°) 1 m^3	= 1.35 (Berthelot and Ogier).
1 kilo.	= 0.65 Cal.

Magnessium Oxide, MgO:

Sm (24°—100°)	= 0.2440 (Regnault).
Sm (0°—t°)	= 0.2420 + 0.000016t (assumed).
Mg (OH^2) Sm (19°—50°)	= 0.312 (Kopp).

Aluminium Oxide, Al^2O^3 (alumina, corundum):

Sm (0° to t°)	= 0.2081 + 0.0000876t (constant by Regnault, coefficient of t by Richards, on a corundum crystal tested up to 1200°).
Melting point	= about 2050°.
Latent heat of fusion	= 2.1T = 4,878 Cal. for Al^2O^3.
	$= \frac{4,878}{102}$ = 48 Cal. per kilo.
Heat in solid at 2050°	= 795 Cal. by formula.
Total heat in liquid to 0°	= 843 Cal.
Specific heat, liquid	= 0.567 = specific heat of solid at M. P.

Silicon Oxide, SiO^2 (silicon, quartz):

Sm (0° to t°)	= 0.1833 + 0.000077t (constant by Regnault, coefficient of t by Richards, on clear quartz up to 1200°).
Latent heat of fusion (at 1750°)	= 135 Cal. (Vogt).
Melting point	= 1900° (Boudouard).
Latent heat of fusion	= 2.1T = 4,563 Cal. for SiO^2.
	$= \frac{4,563}{60}$ = 76.1 Cal. per kilo.
	= 135 Cal. (Vogt).
Heat in solid at 1900°	= 626 Cal. by formula.
Total heat in liquid to 0°	= 761 Cal.
Specific heat, liquid	= 0.476 = specific heat of solid at M. P.

Sulphurous Oxide, SO^2:

Sm (16°—202°) 1 m^3	= 0.4447 (Regnault).
1 kilo.	= 0.1544.

If we assume that the molecular specific heat of SO^2 is 8 Calories (from the rule that the molecular specific heat of a gas at constant pressure is 5+n, where n is the number of atoms in the molecule), we would have

S (at 0°) 1 m^3 $= \frac{8}{22.22}$ = 0.36 Cal.

Combining this with Regnault's value of Sm, we would get the formula

$$\begin{aligned} \text{Sm } (0^\circ \text{ to } t^\circ)\ 1\ m^3 &= 0.36+0.0003t \\ 1 \text{ kilo.} &= 0.125+0.0001t \end{aligned}$$

These values are probably accurate enough for furnace calculations, and are very useful in pyritic smelting and the roasting of sulphide ores. While it is always desirable to have direct determinations of such important quantities, yet when they have never been made it is allowable to work out and use the most probable values.

Sulphuric Oxide, SO^3:

The specific heat of this important gas has not been measured. As an approximation we may assume

$$\begin{aligned} \text{S (at0}^\circ\text{) per molecule} &= 9.0 \text{ Cal. (assumed).} \\ \text{per } m^3 &= 0.405 \text{ Cal.} \\ \text{per kilogram} &= 0.11 \text{ Cal.} \end{aligned}$$

For getting an approximation to Sm we may assume the coefficient of t the same as in NH^3, which contains the same number of atoms and is of analogous formula, and we then have

$$\begin{aligned} \text{Sm } (0^\circ \text{ to } t^\circ) \text{ per molecule} &= 9.0 \quad +0.0036t \\ \text{per } m^3 &= 0.405+0.00017t \\ \text{per kilogram} &= 0.100+0.00004t \end{aligned}$$

Calcium Oxide, CaO (lime):

This important datum has not been determined, but since it is so closely analogous to MgO, an approximation may be obtained by assuming that the molecular specific heats of the two compounds are alike. That for MgO is $0.2440 \times 40 = 9.76$ Calories. That for CaO would therefore be

$$\text{Sm } (24^\circ\text{—}100^\circ) = \frac{9.76}{56} = 0.1743$$

and assuming a usual coefficient of t; for compounds of this type:

$$\text{Sm } (0^\circ\text{—}t^\circ) = 0.1715+0.00007t$$

Titanic Oxide, TiO^2:

S (up to 200°) = 0.1790 (Nilson and Pettersson).
Q (0° to 200°) = 35.8 Cal.
Q (0° to t°) for t over 200° = $35.8+0.1790\ (t-200)+.000055\ (t-200)^2$.

Chromium Oxide, Cr^2O^3:

Sm (10°—99°) = 0.1796 (Regnault).

Manganese Oxides:

MnO Sm (13°—98°) = 0.1570 (Regnault).
Mn^2O^3 Sm (15°—99°) = 0.1620 (Oeberg).
(Manganite) $Mn^2O^3H^2O$
Sm (21°—52°) = 0.1760 (Kopp).
(Pyrolusite) MnO^2
Sm (17°—48°) = 0.1590 (Kopp).

Iron Oxides, Fe^2O^3:

Sm (0°—t°) = $0.1456+0.000188t$ (Regnault and Richards).
Fe^3O^4 Sm (0°—t°) = $0.1447+0.000188t$ (Regnault and Richards).

Nickel Oxide, NiO:

Sm (13°—98°) = 0.1588 (Regnault)

Copper Oxides:

Cu^2O Sm (19°—51°) = 0.1110 (Oeberg).
CuO Sm (12°—98°) = 0.1420 (Regnault).

Zinc Oxide, ZnO:

Sm (0°—t°) (to t = 1000°) = $0.1212+0.0000315t$ (Richards).

Arsenious Oxide, As^2O^3:

Sm (13°—97°) = 0.1276 (Regnault).

Zirconium Oxide, ZrO^2:

Sm (0°—100°) = 0.1076 (Nilson and Pettersson).

Columbic Oxide, Cb^2O^5

Sm (0°—t°) = $0.1037+0.000070t$ (Krüss and Nilson).

Molybdic Oxide, MoO^3:

Sm (21°—52°) = 0.1540 (Kopp).

Tin Oxide, SnO^2:

Sm (16°—98°) = 0.0936 (Regnault).
Sm (0—t) = 0.1050 + 0.000006t (Richards).

Antimonious Oxide, Sb^2O^3:

Sm (18°—100°) = 0.0927 (Neumann).

Tungstic Oxide, WO^3:

Sm (8°—98°) = 0.0798 (Regnault).

Mercuric Oxide, HgO:

Sm (5°—98°) = 0.0518 (Regnault).

Lead Oxide, PbO:

Sm (22°—98°) = 0.0512 (Regnault).

Bismuth Oxide, Bi^2O^3:

Sm (20°—98°) = 0.0605 (Regnault).

Thoric Oxide, Th^2O^3:

Sm (0°—100°) = 0.0548 (Nilson and Pettersson).

For those metallic oxides whose specific heat has not been determined, an approximation to the specific heat can be found by assuming that the metallic atoms in a molecule of oxide have each a specific heat 6.4 Calories, and each atom of oxygen in an oxide molecule has an atomic specific heat of 3.6. As a rough approximation, we can further assume that the mean specific heat from 0° to t° increases 0.04 per cent. for each degree of temperature, so that the above calculated specific heat being from 0° to 100°, we can figure out S at zero and the rate of increase of S or Sm with t.

Example: What is the most probable value of the specific heat of CaO? Since molecule weight is 56, and the molecule may be assumed to have a molecular specific heat of 6.4 + 3.6 = 10.0 Calories, the mean specific heat per kilogram (0°—100°) is 10.0 ÷ 56 = 0.1786. S at zero will then be 0.1786 ÷ 1.04 = 0.1717, and we would have the formulæ:

$$Sm = 0.1717 + 0.000071t$$
$$S = 0.1717 + 0.000142t$$
$$Q = 0.1717t + 0.000071t^2$$

Problem 13.

The Jacobs process of producing artificial emery consists in melting down impure bauxite in an electric furnace, and letting the mass cool. Assume the bauxite to be calcined before use, and to contain

	Per cent.
Alumina	88
Ferric oxide (Fe^2O^3)	5
Silica (SiO^2)	5
Titanic oxide (TiO^2)	2

Required:

(1) The heat necessary to just melt a metric ton of this material at 2000°.

(2) The net electric power theoretically required.

(3) The total electric power actually required.

Solution:

(1) Because of the presence of the impurities the alumina melts easier than it otherwise would. We can, therefore, calculate the heat in the alumina melted at 2000°, and the heat in the others melted at their proper melting points, because they absorb their latent heats of fusion at the lower temperature. Take 1000 kilos. of material.

Heat in 1 kilo. of alumina:

Q (0°—2000°) = 0.2081 (2000) + 0.0000876 (2000)²	= 767	Cal.
L.H.F. at 2000° = 2.1 (2000 + 273) ÷ 102 (mol. wt. Al^2O^3)	= 47	"
Total	= 814	"

Heat in 1 kilo. of ferric oxide

Q (0°—1600°) = 0.1456 (1600) + 0.000188 (1600)² (assumed)	= 713	"
L.H.F. at 1600° = 2.1 (1600 + 273) ÷ 160	= 25	"
Heat in liquid = (2000—1600) × 0.75	= 300	"
Total	= 1038	"

Heat in 1 kilo. of silica:

Q (0°—1900°) = 0.1833 (1900) + 0.000077 (1900)²	= 626	"
L.H.F. (Voigt)	= 135	"
Q (1900°—2000°) liquid = 0.476 × 100	= 48	"
Total	= 809	"

Heat in 1 kilo. of titanic oxide:

$Q\ (0°—2000°) = 35.8+0.1790\ (1800)+0.000055\ (1800)^2$ = 536 Cal.

L.H.F. $= 2.1T = 2.1\ (2000+273) \div 80$ = 59 "

Total = 595 "

Total heat to fuse 1000 kilos.:

Heat in alumina	880×814	= 716,320 Cal.
Heat in ferric oxide	50×1038	= 51,900 "
Heat in silica	50×809	= 40,450 "
Heat in titanic oxide	20×595	= 11,900 "
	Total	= 820,570 "

(2) One kilowatt equals 859 Calories per hour.

$$\text{Kilowatt-hours absorbed by melt} = \frac{820,570}{859} = 955.3 \text{ kw-hr.}$$

(3) Assume an efficiency of 50 per cent., requires 1911 kw-hrs. If the dynamos work at 95 per cent., efficiency, the working power of the water turbine, gas engines or steam engines would be $\frac{1911}{0.95} = 2000$ kw. hr.

Problem 14.

The ferric oxide charged into a blast furnace is reduced at 900° C. by carbonous oxide gas, CO, according to the reaction: $Fe^2O^3+9CO+\ (17.15N^2) = Fe^2+3CO^2+6CO+\ (17.15N^2)$.

Required:

(1) The thermal value of the reaction at 900°.

(2) What would be the temperature of the resulting products after the reaction had occurred?

Solution:

(1) The 6CO and $17.15N^2$ occurring on both sides of the equation need not be considered. The heat value of the equation at *ordinary temperatures* would therefore be:

Decomposition of Fe^2O^3	= —195,600 Cal.
Decomposition of 3CO	= — 87,480 "
Formation of $3CO^2$	= +291,600 "
Thermal value of reaction	= + 8,520 "

At 900°, the value is changed as follows:

Added:

Heat in Fe^2O^3 (160 kilos.) at 900° = 160 [0.1456 (900) + 0.000188 (900)²] = + 45,200 Cal.

Heat in 3CO (= 66.66 m^3) at 900° = 66.66 [0.303 (900) + 0.000027 (900)²] = + 19,640 "

Total to be added = + 64,840 "

Subtracted:

Heat in Fe^2 (112 kilos.) at 900° = 112 × (0.218t—39) = 17,585 "

Heat in $3CO^2$ (66.66 m^3) at 900° = 66.66 [0.37 (900) + 0.00022 (900)²] = 34,080 "

Total to be subtracted 51,665 "

Heat of reaction at 900° = 8,520 + 64,840— 51,665 = + 21,695 "

(2) The above heat would serve to raise the temperature of all the products, viz.: Fe^2, $3CO^2$, 6CO, $17.15N^2$ (from blast).

Their thermal capacity, 900° to t, is:

Fe^2 = 112 [0.218 (t—900)]

$3CO^2$ = 66.66 [0.37 (t—900) + 0.00022 (t^2—900^2)]

6CO = 133.33 [0.303 (t—900) + 0.000027 (t^2—900^2)]

$17.15N^2$ = 17.15 [" "]

Sum = $0.018517t^2 + 94.68t - 100.383$ = 21,695 Calories.

Whence t = 1065°.

It follows from the preceding discussion that the reduction of iron oxide by CO, at about 900°, is an exothermic reaction, heat being evolved, and that the reaction proceeds to a finish when once started. The relations for FeO would be probably similar, but we do not have the specific heat of FeO to use in making the exact calculations.

Problem 15.

If Fe^2O^3 charged into a blast furnace were reduced by solid carbon, at 900° C., by the reaction

$$4Fe^2O^3 + 9C = 3CO^2 + 6CO + 4Fe^2.$$

Required:

(1) The thermal value of the reaction at 900° C

(2) The temperature of the resultant products after the reaction.

Solution:

(1) Value of the reaction at zero	$= -4(195,600)$ Cal.
	$+3(97,200)$
	$+6(29,160)$
Add:	$= -$ 315,840
Heat in $4Fe^2O^3$ at 900°	$= +$ 180,800 "
Heat in 9C at 900° $= 9(12)$ $[0.2142(900) +$ $0.000166(900^2)]$	$= +$ 35,340 "
Subtract:	
Heat in $4Fe^2$ at 900°	$= -$ 70,340 "
Heat in $3CO^2$ at 900°	$= -$ 34,080 "
Heat in 6CO at 900° $= 6$ (22.22) $[0.303$ (900) $+0.000027(900^2)]$	$= -$ 39,275 "
Algebraic sum	$= -$ 243,395 "
Absorbed per molecule of Fe^2O^3	$= -$ 60,850 "

This reaction is therefore strongly endothermic, and therefore tends to check itself constantly by the resultant cooling effect.

(2) If the Fe^2O^3 and C were at 900° to start with, the products would be below 900° after the reaction, since they would have to furnish the deficit of heat.

The products would give out in cooling from 900° to t°.

$4Fe^2 = 4(112)\ [0.218(900—t)]$
$3CO^2 = 66.66\ \ [0.37(900—t) + 0.00022(900^2—t^2)]$
$6CO = 133.33\ \ [0.303(900—t) + 0.000027(900^2—t^2)]$
Sum $= 0.0183t^2$——$162.73t + 161,250, = 243,395$ Cal.
Whence $t = -537°$.

This result is, of course, due to the hypothetical assumption that this endothermic reaction would go on until completed without checking itself. The impossible result obtained means that if this single reaction really goes on, it will soon check itself on account of the decrease of temperature.

There are a few other compounds than those previously mentioned whose thermophysics has been investigated, but their number is in reality infinitesimal compared with the number of those which have not been touched. There are many

compounds of great importance in metallurgy whose specific heats are not known, to say nothing of their latent heats of fusion, etc. The wide introduction of the electric furnace has rendered desirable the latent heats of vaporization and specific heats at high temperatures, but these are altogether lacking; we can only estimate their values. It is to be hoped that many metallurgical laboratories may be incited to take up this very neglected field, and thus bring forward numerical data which would be of the greatest theoretical and practical value. One example of such work, which deserves special commendation, is the quite recent publication of Prof. J. H. L. Vogt, of Christiania, on the "Silikatschmelzlösungen," *i.e.*, on "Melted Silicate Solutions," in which determinations of the melting points and latent heats of fusion of many simple and complex silicates are given for the first time; we venture to predict that the data and conclusions of Prof. Vogt will be of great value to the physicist, chemist, metallurgist, and geologist, in both a practical as well as a theoretical sense.

In collating the remaining available data, it is rather difficult to decide as to what has immediate metallurgical interest and what has not. Electrometallurgy, in particular, is busying itself with the treatment and decomposition of so many compounds heretofore considered outside of the metallurgist's sphere of interest, that almost all of the common chemical compounds now have either a present or a prospective interest to the metallurgist.

THERMOPHYSICS OF CHLORIDES

Substance	*Temperature*	*Specific Heat*	*L. H. Fusion*	*L. H. Vaporization*	*Authority*
HCl (gas)	22–214°	0.1867	.....	.....	Regnault
		0.3067(1m³)			
HCl (liquid)	−83	.....	.....	97.5	Elliott & McIntosh
RbCl (fused)	16–45	0.112	.....	.....	Kopp
LiCl (fused)	13–97	0.2821	.....	.....	Regnault
KCl	14–99	0.1730	.....	.....	Regnault
KCl	772	.....	86.0	.....	Plato
NaCl	15–98	0.2140	.....	.....	Regnault
NaCl	804	.....	123.5	.....	Plato
NH_4Cl	23–100	0.3908	.....	.....	Neumann

Substance	Temperature	Specific Heat	L. H. Fusion	L. H. Vaporization	Authority
NH_4Cl	350°	.....	.....	709	Marignac
$BaCl_2$ (fused)	14–98	0.0896	.....	.....	Regnault
$BaCl_2$ (fused)	959	.....	27.8	.....	Plato
$SrCl_2$	13–98	0.1199	.....	.....	Regnault
$SrCl_2$	872	.....	25.6	.....	Plato
$CaCl_2$ (fused)	23–99	0.1642	.....	.....	Regnault
$CaCl_2$ (fused)	774	.....	54.6	.....	Plato
$MgCl_2$ (fused)	24–100	0.1946	.....	.....	Regnault
$AlCl_3$	−22–15	0.188	.....	.....	Band
$TiCl_4$ (solid)	13–99	0.1881	.....	.....	Regnault
$TiCl_4$ (gas)	163–271	0.1290	.....	.....	Regnault
$SiCl_4$ (liquid)	10–15	0.1904	.....	.....	Regnault
$SiCl_4$ (gas)	90–234	0.1322	.....	.....	Regnault
$SiCl_4$ (gas)	90–234	$1.0113(1m^3)$	.....	.....	Regnault
$SiCl_4$ (liquid)	?	.....	.....	37.3	Ogier
CCl_4 (liquid)	20°	0.207	.....	.....	Timofejew
CCl_4 (liquid)	0°	.....	.....	52.0	Regnault
$MnCl_2$	15–98(?)	0.1425	.....	.....	Regnault
$MnCl_2$ (liquid)	?	.....	.....	49.4(?)	Ogier.
$ZnCl_2$ (fused)	21–99	0.1362	.....	.....	Regnault.
TlCl (solid)	0–t	0.0525 +0.000007t	....	....	Russell, Goodwin & Kalmus
TlCl (at M. P.)	427°	0.0585	.....	.....	
TlCl (solid)	427°	.....	16.6	.....	
TlCl (liquid)	427–530	0.0590	.....	.....	
$CrCl_2$	?	0.1430	.....	.....	Kopp
PCl_3 (solid)	11–98	0.2092	.....	.....	Regnault
PCl_3 (liquid)	78.5	.....	.....	51.42	Andrews
PCl_3 (gas)	111–246	0.135	.....	.....	Regnault
$AsCl_3$ (liquid)	14–98	0.1760	.....	.....	Regnault
$AsCl_3$ (liquid)	.....	.....	.....	69.74	Regnault
$AsCl_3$ (gas)	159–268	0.1122	.....	.....	Regnault
$SnCl_2$ (fused)	20–99	0.1016	.....	.....	Regnault
$SnCl_4$ (liquid)	10–15	0.1904	.....	.....	Regnault
$SnCl_4$ (liquid)	112	.....	.....	46.84	Regnault
$SnCl_4$ (gas)	149–273	0.0939	.....	.....	Regnault
HgCl (solid)	7–99	0.0521	.....	.....	Regnault
$HgCl_2$ (solid)	13–98	0.0689	.....	.....	Regnault
CuCl (solid)	17–98	0.1383	.....	.....	Regnault
$PbCl_2$ (solid)	0–t	0.0630 +0.000021t	.....	.....	Lindner, Goodwin & Kalmus
$PbCl_2$ (at M. P.)	498	0.0839	.....	.....	
$PbCl_2$ (solid)	498	.....	18.5	.....	
$PbCl_2$ (liquid)	> 498	0.1035	.....	.....	Ehrhardt
AgCl (fused)	0-t	0.0897 +0.0000125t	....	....	Regnault Goodwin,

Substance	Temperatur	Specific Heat	L. H. Fusion	L. H. Vaporization	Authority
AgCl (at M. P.)	455°	0.1011	.....	.....	Robertson & Kalmus
AgCl (solid)	455	.....	30.5	.....	
AgCl (liquid)	455–533	0.129	.....	.....	
Thermophysics of Bromides					
HBr (gas)	11–100	0.0820	.....	.....	Strecker
HBr (gas)	11–100	0.2989 (per m³)	.....	.....	Strecker
HBr (liquid)	–70	.....	.....	48.68	Estreigher & Schnerr
KBr (fused)	16–98	0.1132	.....	.....	Regnault
NaBr	0–96	0.1170	.....	.....	Koref
$AlBr_3$	93°	.....	10.47	.....	Kablukow
$SbBr_3$	95	.....	9.76	.....	Telloczko
$AsBr_3$	31	.....	8.93	.....	Telloczko
$SnBr_4$	30	.....	6.26	.....	Telloczko
TlBr	460	.....	12.7	.....	Goodwin & Kalmus
$PbBr_2$ (fused)	0–t	0.0526	.....	.....	Goodwin & Kalmus
		+0.000006t	.....	.....	
$PbBr_2$ (at M. P.)	488	0.0585	.....	.....	from formula
$PbBr_2$ (at M. P.)	488	.....	9.9	.....	G. & K.
$PbBr_2$ (at M. P.)	488	.....	12.34	.....	Ehrhardt
$PbBr_2$ (liquid)	488–587	0.0780	.....	.....	G. & K.
AgBr (fused)	0–t	0.0736	.....	.....	Regnault, Goodwin & Kalmus.
		+0.0000025t	.....	.....	
AgBr (at M. P.)	430	0.0757	.....	.....	Calculated
AgBr (at M. P.)	430	.....	12.6	.....	G & K.
AgBr (liquid)	430–563	0.0760	.....	.....	G. & K.
Thermophysics of Iodides					
HI (gas)	21–100	0.0550	.....	.....	Strecker
HI (gas)	21–100	0.3168 (per m³)	.....	.....	Strecker
HI (liquid)	–37	.....	.....	35.00	Elliott & McIntosh
KI (solid)	13–48	0.0766	.....	.....	Nernst
NaI (solid)	16–99	0.0868	.....	.....	Regnault
CuI (solid)	18–99	0.0687	.....	.....	Regnault
Hg_2I (red)	0–100	0.0406	.....	.....	Guinchant
Hg_2I (yellow)	0–247	0.0446	.....	.....	Guinchant
Hg_2I (liquid)	250–327	0.0554	.....	.....	Guinchant
HgI (solid)	17–99	0.0395	.....	.....	Regnault
HgI_2 (solid)	18–99	0.0420	.....	.....	Regnault
HgI_2 (at M. P.)	250	.....	9.79	.....	Guinchant

Substance	Temperature	Specific Heat	L. H. Fusion	L. H. Vaporization	Authority
PbI_2 (solid)	0–375°	0.0430	.....	.....	Ehrhardt
PbI_2 (at M. P.)	375	.....	11.50	.....	Ehrhardt
PbI_2 (liquid) >	375	0.0645	.....	.....	Ehrhardt
AgI (solid)	15–264	0.0577	.....	.....	Bellati & Romanese
PbI_2.AgI	10–124	0.0476	.....	.....	Bellati & Romanese
Thermophysics of Fluorides					
HF (liquid)	?	.....	....	360	Guntz
KF	−76–0	0.1930	....	.....	Koref
KF (M. P.)	860	.....	108	.....	Plato
NaF	15–53	0.2675	.....	.....	Band
$3NaF.AlF_3$ (Cryolite)	16–99	0.2522	.....	.....	Oeberg
CaF_2	15–99	0.2154	.....	.....	Regnault
AlF_3	15–53	0.2294	.....	.....	Band
$AlF_3.7H_2O$	15–53	0.342	.....	.....	Band
PbF_2	0–34	0.0722	.....	.....	Schottky
Thermophysics of Sulfides					
H_2S (gas)	20–206	0.2451	.....	.....	Regnault
H_2S (gas)	20–206	0.3750(1m³)	.....	.....	Regnault
H_2S (gas)	0–t	(1m³)0.34 +0.00015t	.....	.....	Richards
CS_2 (liquid)	14–29	0.2468	.....	.....	Person
CS_2 (gas)	86–190	0.1596	.....	.....	Regnault
CS_2 (gas)	86–190	0.5458(1m³)	.....	.....	Regnault
CS_2 (liquid)	46	.....	83.8	.....	Wirtz
MnS	10–100	0.1392	....	.....	Sella
ZnS	15–98	0.1230	.....	.....	Regnault
CdS	26	0.0908	.....	.....	Russell
FeS	17–98	0.1357	.....	.....	Regnault
Fe_7S_8 (Pyrrhotite)	20–100	0.1602	.....	.....	Regnault
FeS_2	19–98	0.1301	.....	.....	Regnault
FeS_2	565	(Gives off S)	.....	.....	Richards
CoS	15–98	0.1251	.....	.....	Regnault
NiS	15–98	0.1281	.....	.....	Regnault
MoS_2 (Molybdenite)	20–100	0.1233	.....	.....	Regnault
Cu_2S (Chalcocite)	9–97	0.1212	.....	.....	Regnault
	103	Transformation Point	.....	.....	Bellati & Lussana
	190	0.1454	.....	.....	Bellati & Lussana

Substance	*Temperature*	*Specific Heat*	*L. H. Fusion*	*L. H. Vaporization*	*Authority*
CuS (Covellite)	25°	0.1243	.....	.....	Russell
AsS (Realgar)	20–100	0.1111	.....	.....	Naumann
As_2S_3 (Orpiment)	20–100	0.1132	.....	.....	Naumann
(Orpiment) (gas)	0–t	(1 m^3)0.34 +0.00015t	.....	.....	Richards
Sb_2S_3 (Stibnite)	23–99	0.0840	.....	.....	Regnault
SnS	13–98	0.0837	.....	.....	Regnault
SnS_2	12–95	0.1193	.....	.....	Regnault
PbS	16–98	0.0509	.....	.....	Regnault
PbS (liquid)	1050	.....	50 (104 to 0°)	.....	Richards
Bi_2S_3 (fused)	11–99	0.0600	.....	.....	Regnault
HgS	14–98	0.0512	.....	.....	Regnault
Ag_2S	7–98	0.0746	.....	.....	Regnault
Ag_2S	0–t	0.0685 +0.00005t	.....	.....	Bellati & Lussana

THERMOPHYSICS OF COMPOUND SULFIDES

$3Cu_2S.Fe_2S_3$ (Bornite)	10–100	0.1177	.....	.....	Sella
$Cu_2S.Fe_2S_3$ (Chalcopyrite)	14–98	0.1310	.....	.....	Kopp
(Chalcopyrite)	720	(Gives off S)	.....	.....	Richards
Cu Matte (47% Cu)	0–t	0.2110 −0.0000366t	.....	.....	Landis
Cu Matte (47% Cu)	1000°	.....	30	.....	Landis
Cu Matte (liquid)	1000°	.....	(204 to 0°)	.....	Landis
$4Cu_2S.Sb_2S_3$ (Tetrahedrite)	10–100	0.0987	.....	.....	Sella
$2PbS.Cu_2S.Sb_2S_3$ (Bournonite)	10–100	0.0730	.....	.....	Sella
$FeS_2.FeAs_2$ (Arsenopyrite)	10–100	0.1030	.....	.....	Sella
$CoS_2.CoAs_2$ (Cobaltite)	15–99	0.0991	.....	.....	Sella
$3Ag_2S.As_2S_3$	10–100	0.0807	.....	.....	Sella
$3Ag_2S.Sb_2S_3$	10–100	0.0757	.....	.....	Sella

THERMOPHYSICS OF SELENIDES AND TELLURIDES

Substance	Temperature	Specific Heat	L. H. Fusion	L. H. Vaporization	Authority
Cu_2Se	20–200°	0.1047	.....	.....	Bellati & Lussana
Ag_2Se	37–187	0.0684	.....	.....	

THERMOPHYSICS OF ARSENIDES AND ANTIMONIDES

$FeAs_2$ (Löllingite)	10–100	0.0864	.....	.....	Sella
$CoAs_2$ (Smaltite)	10–100	0.0830	.....	.....	Sella
Cu_3As (Domeykite)	10–100	0.0949	.....	.....	Sella
Ag_3Sb (Dyscrasite)	10–100	0.0558	.....	.....	Sella

THERMOPHYSICS OF CYANIDES

$K_4Fe(CN)_6$	1–46	0.2142	.....	.....	Nernst
$K_2Zn(CN)_2$	14–46	0.241	.....	.....	Kopp
$Hg(CN)_2$(cryst)	11–46	0.100	.....	.....	Kopp

THERMOPHYSICS OF HYPOSULFITES

$K_2S_2O_3$	20–100	0.197	.....	.....	Pape
$Na_2S_2O_3$	25–100	0.221	.....	.....	Pape
BaS_2O_3	17–100	0.163	.....	.....	Pape
PbS_2O_3	15–100	0.092	.....	.....	Pape

THERMOPHYSICS OF SULFATES

H_2SO_4	10.5	.....	26.0	.....	Brönsted
H_2SO_4	5–22	0.332	.....	.....	Cattanes
H_2SO_4	326	.....	.....	122.1	Person
K_2SO_4	15–98	0.1901	.....	.....	Regnault
$KHSO_4$	19–51	0.2440	.....	.....	Kopp
Na_2SO_4	17–98	0.2312	.....	.....	Regnault
$Na_2SO_4.10H_2O$	31	.....	51.2	.....	Cohen
$BaSO_4$	10–98	0.1128	.....	.....	Regnault
$SrSO_4$	21–99	0.1428	.....	.....	Regnault
$CaSO_4$	13–98	0.1965	.....	.....	Regnault
$MgSO_4$	25–100	0.2250	.....	.....	Pape
$Al_2K_2(SO_4)_3.24H_2O$	15–52	0.3490	.....	.....	Band
$(NH_4)_2SO_4.12H_2O$	13–45	0.3500	.....	.....	Kopp
$ZnSO_4$	22–100	0.1740	.....	.....	Pape
$MnSO_4$	21–100	0.1820	.....	.....	Pape
$Cr_2K_2(SO_4)_4.24H_2O$	19–51	0.3240	.....	.....	Kopp

Substance	*Temperature*	*Specific Heat*	*L. H. Fusion*	*L. H. Vaporization*	*Authority*
$FeSO_4.7H_2O$	9–16°	0.3460	.....	.....	Kopp
$CoSO_4.7H_2O$	15–80	0.3430	.....	.....	Kopp
$NiSO_4$	15–100	0.1840	.....	.....	Pape
$CuSO_4$	23–100	0.1840	.....	.....	Pape
$PbSO_4$	20–99	0.0872	.....	.....	Regnault
Hg_2SO_4	0–34	0.0624	.....	.....	Schottky
		THERMOPHYSICS OF NITRATES			
HNO_3	−47	.....	9.54	.....	Berthelot
HNO_3	86	.....	.....	115.1	Berthelot
$LiNO_3$	169–250	0.387	.....	.....	Goodwin & Kalmus
$LiNO_3$	250	.....	88.5	.....	Goodwin & Kalmus
$LiNO_3$ (liquid)	250–302	0.390	.....	.....	Goodwin & Kalmus
KNO_3	13–98	0.239	.....	....	Regnault
KNO_3	334°	.....	48.9	.....	Person
KNO_3 (liquid)	350–435	0.332	.....	.....	Person
$NaNO_3$	14–98	0.278	.....	.....	Regnault
$NaNO_3$	306	.....	64.9	.....	Person
$NaNO_3$ (liquid)	320–430	0.413	.....	.....	Person
$K_2Na(NO_3)_2$	15–100	0.235	.....	.....	Person
NH_4NO_3	14–31	0.455	.....	.....	Kopp
$BaNO_3$	13–98	0.1523	.....	.....	Regnault
$SrNO_3$	17–47	0.181	.....	.....	Kopp
$CaNO_3.4H_2O$	42	.....	33.5	.....	Pickering
$AgNO_3$	16–99	0.1435	.....	.....	Regnault
$AgNO_3$	209	.....	17.6	.....	Guinchant
$AgNO_3$ (liquid)	208–281	0.187	.....	.....	Guinchant
$PbNO_3$	17–100	0.1173	.....	.....	Neumann
		THERMOPHYSICS OF CARBONATES			
Pb_2CO_3 (fused)	18–47	0.123	.....	.....	Kopp
K_2CO_3	23–99	0.2162	.....	.....	Regnault
Na_2CO_3	16–98	0.2728	.....	.....	Regnault
$BaCO_3$	11–99	0.1104	.....	.....	Regnault
$SrCO_3$	8–98	0.1475	.....	.....	Regnault
$CaCO_3$ (calcite)	20–100	0.2086	.....	.....	Regnault
$CaCO_3$ (argonite)	18–99	0.2085	.....	.....	Regnault
$CaCO_3$ (marble)	23–98	0.2099	.....	.....	Regnault
$CaMg(CO_3)_2$ (Dolomite)	20–100	0.2179	.....	.....	Regnault
$Mg_7Fe_2(CO_3)_9$ (Brown magnesite)	17–100	0.2270	.....	.....	Neumann

Substance	Temperature	Specific Heat	L. H. Fusion	L. H. Vaporization	Authority
$ZnCO_3$	0–t°	$\left\{\begin{matrix}0.1407\\+0.0001t\end{matrix}\right\}$	.....	.....	Lindner
$CuCO_3.Cu(OH)_2$ (Malachite)	15–99	0.1763	.....	.....	Oeberg
$FeCO_3$	9–98	0.1935	.....	.....	Regnault
$PbCO_3$	16–47	0.0791	.....	.....	Kopp
		THERMOPHYSICS OF CHROMATES			
K_2CrO_4	19–98	0.1851	.....	.....	Regnault
$K_2Cr_2O_7$	0–t	$\left\{\begin{matrix}0.1803\\+0.00008t\end{matrix}\right\}$	.....	.....	Regnault, & Goodwin & Kalmus
$K_2Cr_2O_7$	397	.....	29.8	.....	Goodwin & K.
$K_2Cr_2O_7$ (liquid)	397–484	0.335	.....	.....	Goodwin & K.
Na_2CrO_4	23	.....	39.2	.....	Berthelot
$FeCrO_4$ (Chromite)	19–50	0.1590	.....	.....	Kopp
$PbCrO_4$	19–50	0.0900	.....	.....	Kopp
		THERMOPHYSICS OF BORATES			
$K_2B_2O_4$	16–98	0.2048	.....	.....	Regnault
$K_2B_4O_7$	18–99	0.2198	.....	.....	Regnault
$Na_2B_2O_4$	17–97	0.2571	.....	.....	Regnault
$Na_2B_4O_7$	16–98	0.2382	.....	.....	Regnault
PbB_2O_4	15–98	0.0905	.....	.....	Regnault
PbB_4O_7	16–98	0.1141	.....	.....	Regnault
		THERMOPHYSICS OF PHOSPHATES			
H_3PO_4	18	.....	25.71	.....	Thomsen
$K_4P_2O_7$	17–98	0.1910	.....	.....	Regnault
$Na_4P_2O_7$	17–98	0.2283	.....	.....	Regnault
CaP_2O_5	15–98	0.1992	.....	.....	Regnault
$3Ca_3P_2O_8.CaF_2$ (Apatite)	15–99	0.1903	.....	.....	Oeberg
$Pb_2P_2O_7$ (fused)	11–98	0.0821	.....	.....	Regnault
$Pb_3P_2O_8$	11–98	0.0798	.....	.....	Regnault
Ag_3PO_4	19–50	0.0898	.....	.....	Kopp
		THERMOPHYSICS OF ARSENATES			
$Pb_3As_2O_8$ (fused)	13–97	0.0728	.....	.....	Regnault
$K_2As_2O_6$ (fused)	17–99	0.1563	.....	.....	Regnault

Thermophysics of Chlorates and Per-chlorates

Substance	*Temperature*	*Specific Heat*	*L. H. Fusion*	*L. H. Vaporization*	*Authority*
$KClO_3$ (fused)	16–98°	0.2096	.....	.....	Regnault
$KClO_4$	14–45	0.190	.....	.....	Kopp
$NaClO_3$ (fused)	184–255	0.320	.....	.....	Goodwin & Kalmus
$NaClO_3$ (fused)	255	.....	49.6	.....	Goodwin & Kalmus
$NaClO_3$ (liquid)	255–299	0.325	.....	.....	Goodwin & Kalmus

Thermophysics of Aluminates

$MgAl_2O_4$ (Spinel)	15–47	0.1940	.....	.....	Kopp
$BeAl_2O_4$ (Chrysoberyl)	0–100	0.2004	.....	.....	Nilson & Petersson

Thermophysics of Titanates

$FeTiO_3$	15–50	0.177	.....	.....	Kopp

Thermophysics of Molybdates

$PbMoO_4$ (Wulfenite)	15–50	0.083	.....	.....	Kopp

Thermophysics of Tungstates

$CaWO_4$ (Scheelite)	15–50	0.097	.....	.....	Kopp
$Fe(Mn)WO_4$ (Wolframite)	15–50	0.098	.....	.....	Kopp

Thermophysics of Manganates

$KMnO_4$	15–50	0.179	.....	.....	Kopp

Thermophysics of Silicates

Mg_2SiO_4 (Olivin)	0–100	0.2200	.....	.....	Vogt

Substance	Temperature	Specific Heat	L. H. Fusion	L. H. Vaporization	Authority
Mg_2SiO_4 (Olivin)	1400°	.....	130	.....	Vogt
Mg_2SiO_4 (liquid)	1400	.....	[520 to 0°]	.....	Vogt
$MgSiO_3$ (Enstatite)	0–t	0.1974 +0.000086t	.....	.....	Vogt
$MgSiO_3$ (Enstatite)	1300	.....	125	.....	Vogt
$MgSiO_3$ (liquid)	1300	.....	[403 to 0°]	.....	Vogt
$CaSiO_3$ (Wollastonite)	0–t	0.1690 +0.0001t	.....	.....	Vogt
$CaSiO_3$ (Wollastonite)	1250	.....	100	.....	Vogt
$CaSiO_3$ (liquid)	1250	.....	[360 to 0°]	.....	Vogt
$CaMgSi_2O_6$	0–t	0.186 +0.00008t	.....	.....	Vogt
$CaMgSi_2O_6$	1225	.....	100	.....	Vogt
$CaMgSi_2O_6$ (liquid)	1225	.....	[344 to 0°]	.....	Vog
$Ca_3MgSi_4O_{12}$ (Malacolite)	0–t	0.179 +0.00007t	.....	.....	Vog
$Ca_3MgSi_4O_{12}$	1200	.....	94	.....	Vogt
$Ca_3MgSi_4O_{12}$ (liquid)	1200	.....	[319 to 0°]	.....	Vogt
$H_4Al_2Si_2O_9$ (Kaolin)	20–98	0.2243	.....	.....	Ulrich
$Al_2Si(F)O_5$ (Topaz)	12–100	0.1997	.....	.....	Joly
$KAlSi_3O_8$ (Orthoclase)	20–100	0.1877	.....	.....	Oeber
$KAlSi_3O_8$ (Orthoclase)	1200	.....	100	.....	Vogt
$KAlSi_3O_8$ (Microcline)	20–100	0.197	.....	.....	Bogajawlensky
$KAlSi_3O_8$ (Microcline)	1170	.....	83	.....	Vogt
$CaAl_2Si_2O_8$ (Anorthite)	0–t	0.1790 +0.0001t	.....	.....	Vogt
$CaAl_2Si_2O_8$ (Anorthite)	1220	.....	100	.....	Vogt
$CaAl_2Si_2O_8$ (liquid)	1220	.....	[358 to 0°]	.....	Vogt

Substance	*Temperature*	*Specific Heat*	*L. H. Fusion*	*L. H. Vaporization*	*Authority*
$ZrSiO_4$ (Zircon)	15–100°	0.1456	.....	.....	Regnault
$BeAl_2Si_2O_8$ (Beryl)	12–100	0.2066	.....	.....	Joly
$Fe_3Al_2Si_3O_{12}$ (Iron Garnet)	16–100	0.1758	.....	.....	Oeberg
Al_2SiO_5 (Audalusite)	0–100	0.1684	.....	.....	Lindner
Asbestos	20–98	0.1947	.....	.....	Ulrich
Serpentine	16–98	0.2586	.....	.....	Oeberg
Talc (soapstone)	20–98	0.2092	.....	.....	Ulrich
Potash mica	20–98	0.2080	.....	.....	Ulrich
Sodium mica	20–98	0.2085	.....	.....	Ulrich
Magnesia mica	20–98	0.2061	.....	.....	Ulrich
Oligoclase	20–98	0.2048	.....	.....	Ulrich
Spodumene	20–100	0.2176	.....	.....	Schulz
Labradorite	20–98	0.1949	.....	.....	Ulrich
Hypersthene	20–98	0.1914	.....	.....	Ulrich
Augite	20–98	0.1931	.....	.....	Ulrich
Hornblende	20–98	0.1952	.....	.....	Ulrich
Granite	20–524	0.2290	.....	.....	Bartoli
Basalt	0–t	0.1937 +0.000086t	.....	.....	Bartoli
Basalt	?		130	.....	Tamman
Lava (Etna)	0–500	0.1820 +0.000155t	.....	.....	Bartoli
Lava (Etna)	500–800	0.270	.....	.....	Bartoli
Pumice	10–100	0.240	.....	.....	Dunn
Ca, K, Glass	14–99	0.198	.....	.....	Regnault
Ca, K, Glass	0–300	0.190	.....	.....	Dulong & Petit
Flint Glass	10–50	0.117	.....	.....	H. Meyer
Flint Glass	18–100	0.082	.....	.....	Winkelmann
Crown Glass	10–50	0.161	.....	.....	H. Meyer
Mirror Glass	10–50	0.186	.....	.....	H. Meyer
Thermometer glass (French, hard)	.....	0.1869	.....	.....	Zonboff
Jena Glass	18–99	0.2182	.....	.....	Winkelmann
Thermometer glass (Normal, German)	19–100	0.1988	.....	.....	Winkelmann
Porcelain	0–t	0.2826 −0.0000264t	.....	.....	Harker
Cement clinker	28–40	0.186	.....	.....	Hartl
Portland cement	28–30	0.271	.....	.....	Hartl
Humus (soil)	20–98	0.443	.....	.....	Ulrich
Quartz sand	20–98	0.1910	.....	.....	Ulrich

Substance	*Temperature*	*Specific Heat*	*L. H. Fusion*	*L. H. Vaporization*	*Authority*
Sandstone	0–100°	0.174	.....	.....	Hecht
Slag	14–99	0.1888	.....	.....	Oeberg
Enamel slag	15–99	0.1865	.....	.....	Oeberg
Bessemer slag	14–99	0.1691	.....	.....	Oeberg
		MISCELLANEOUS MATERIALS			
Paraffin (solid)	0–t	0.532 +0.0012t	.....	.....	Battelli
Paraffin (liquid)	52–63	0.706	.....	.....	Battelli
Beeswax (solid)	26–42	0.82	.....	.....	Person
Beeswax (liquid)	65–100	0.50	.....	.....	Person
Soft Para Rubber	0–100	0.48	.....	.....	Gee & Terry
Vulcanite	20–100	0.331	.....	.....	A. M. Mayer
Anthracite	0–12	0.312	.....	.....	Hecht
Oak Wood	.....	0.57	.....	.....	——
Fir Wood	.....	0.65	.....	.....	——
Charcoal	.....	0.20			——
Red Brick	.....	0.22			——
Ether	25	0.54	.....	.....	Regnault
Ether	35	.....	.....	90	Brix
Alcohol	20–26	0.58	.....	.....	Bose
Alcohol (liquid)	78	.....	.....	206	Schall
Benzol (liquid)	10	0.40	.....	.....	Pickering
Benzol (solid)	5	.....	30	.....	J. Meyer
Benzol (liquid)	80	.....	.....	94	Tyrer
Glycerin	.....	0.58			——
Glycerin	13	.....	42.5	.....	Berthelot
Machine oil	.....	0.40			——
Petroleum	.....	0.50			——
Turpentine	.....	0.42			——
Turpentine	159	.....	.....	74	Brix
Stearic acid	64	.....	47.6	.....	Bruner
Ammonia (gas)	0–t	0.38 +0.00016t	.....	.....	LeChatelier
Ammonia (solution)	18	1.00	.....	.....	Thomsen
Ammonia (liquid)	16	.....	.....	297	Regnault
Methane (CH_4)	0–t	0.38 +0.00022t			
Ethelyne (C_2H_4)	0–t	0.46 +0.0003t	.....	.....	LeChatelier

For silicates in general, the specific heat is found to agree fairly well with what would be calculated from their percent-

age composition, giving each oxide constituent its proper specific heat. Those oxides whose specific heat at 0° are known are as follows:

SiO^2 = 0.1833 (Richards)
Al^2O^3 = 0.2081 (Richards).
Fe^2O^3 = 0.1456 (Richards).
MgO = 0.2420 (Regnault).
CaO = 0.1779 (calculated).

Those which are not known give good results if assumed to be as follows:

FeO = 0.1460 (Vogt).
MnO = 0.1511 (Vogt).
K^2O = 0.1390 (Vogt).
Na^2O = 0.2250 (Vogt).
Li^2O = 0.4430 (Vogt).

Using these data, S at 0° is calculated from the percentage composition of the silicate. For S at higher temperatures it can be assumed with considerable approximation to the truth, that S increases 0.078 per cent. for each degree, and so, calling S_0 the specific heat at zero, we would have

$S = S_0 (1+0.00078t)$
$Sm = S_0 (1+0.00039t)$
$Q\ (0°—t°) = Sm \times t$

Besides the above generalizations, which enable one to calculate the heat in the solid silicate at the melting point (when the latter is known), Vogt has shown that if the heat necessary to heat the silicate from—273° to the melting point is calculated, the latent heat of fusion may be taken as being 20 to 25 per cent. of this quantity, say an average of 22.5 per cent. and thus the heat required for fusion may be approximately calculated.

Akerman has determined for many metallurgical silicate slags the total heat contained per kilogram of melted slag at the melting point. These quantities vary from 347 to 530 Calories, depending principally on the elevation of the melting point of the slag. A brief tabulation of Akerman's results are as follows, arranged according to the amount of heat in the just-melted slag:

Calories.	$\%SiO^2$	%CaO	$\%Al^2O^3$
347	59	36	5
	39	42	19
350	63	35	2
	58	35	7
	58	37	5
	53	37	10
	41	42	17
	38	47	15
	39	43	19
	37	40	23
360	66	32	2
	59	38	3
	48	42	10
	40	48	12
	34	48	18
	31	37	32
	46	37	17
	58	32	10
380	58	27	15
	62	37	1
	38	52	10
	25	34	41
	44	33	23
400	60	20	20
	65	35	0
	41	52	7
	37	53	10
	21	32	47
	43	30	27

The above includes most varieties of acid and basic iron blast-furnace slags. Data for other slags made in the metallurgy of iron and of other metals, are almost altogether lacking. A wide field is here open for metallurgical experiments; data thus obtained would be immediately useful in practical calculations.

CHAPTER VI.

ARTIFICIAL FURNACE GAS.

There are many different forms of producers for making artificial furnace gas. For the purposes of making calculations upon them they may be conveniently divided into four classes, as follows:

1. Simple producers, those which use ordinary fuels, such as wood, peat, lignite, bituminous coal or anthracite, and in which no water or water vapor is introduced other than the water in the fuel itself and the normal moisture of the air used.

2. Mixed gas producers, in which water vapor or steam is introduced with the air for combustion, in such amount as to be entirely decomposed in passing through the fuel.

3. Mond gas producers, in which, for a special purpose, more steam is introduced than can be decomposed in the producer, thus producing very wet gas.

4. Water gas producers, in which air and steam alone are alternately fed to the producer, the former for heating up, the latter for producing water gas.

As far as the calculations are concerned, the essential difference between these classes is the varying amount of water vapor or steam introduced under the fuel bed while producing the gas, from all air in Class 1 to all steam in Class 4.

The calculations which it is of immediate interest to make, and the results of which are of immediate value to the metallurgist, are those concerned with the volume of gas produced per unit of fuel, its calorific power compared to that of the fuel from which it is produced, the items of the heat losses during the operation of transforming the solid fuel into gaseous fuel, the function of steam in the producer, the limits up to which the use of steam is permissible, the increase of efficiency of the gas by subsequently drying it, the advantages as to final efficiency which are gained by gasifying the fuel over burning solid fuel directly.

For information as to the construction and operation of gas producers, reference may be made to treatises such as Sexton's or Wyer's "Producer Gas," Groves and Thorp's "Chemical Technology, Vol. V., Fuels." Trade pamphlets and catalogues, such as those of R. D. Wood and Co. on "Gas Producers," of the De la Vergne Machine Co. on "Koerting Gas Engines and Gas Producers," etc., contain a great deal of exact and useful information, and may be usually had for the asking. The monograph of Jüptner and Toldt on "Generatoren und Martinöfen" (Felix, Leipzig, 1900), is concerned wholly with calorimetric calculations concerning the production of gas and its utilization in regenerative gas furnaces.

1.—Simple Producers.

In these a deep bed of fuel is burnt by air or fan blast, introducing no more moisture than happens to be in the atmosphere at the time being. The fuel fed into the producer is first dried by the hot gases, then is heated and distilled or coked, and finally is oxidized by the incoming air. The residue is the ash of the coal, which is ground out at the bottom or drops through the grate, containing more or less unburnt fixed carbon. Great loss of efficiency sometimes occurs from the ashes being rich in carbon. The escaping gases issue at temperatures of 300° up to 1000° C., carrying much sensible heat out of the producer.

Calculations as to the amount of gas produced per unit of fuel consumed are to be based entirely on the carbon. The gas must be carefully analyzed, so that it can be calculated from this analysis how much carbon, in weight, is contained in a given volume of gas. (An alternative method is to take a carefully measured volume of the gas, mix it with excess of oxygen, and explode in a gas burette, determining the amount of carbon dioxide formed, and from that calculate the weight of carbon in the volume of gas taken.) Knowing this, the rest is simple; the carbon in unit weight of fuel minus the carbon lost in the ashes by poor combustion gives the weight of carbon gasified; this divided by the weight of carbon in unit volume of gas produced, gives the volume of the latter per unit weight of fuel.

Illustration: A fuel used in a gas producer contains 12 per

cent. of *ash* and 72 per cent. of carbon. The *ashes* made contain 20 per cent. of unburnt carbon; the gas produced contains by analysis and calculation 0.162 ounce of carbon per cubic foot of gas, measured at 60° F. and 29.8 inches barometric pressure. What volume of gas, measured at above conditions, is being produced per ton of 2240 pounds of coal used?

Solution: The distinction between *ash* and *ashes* must be noted; the former is the analytical expression for the amount of inorganic material left after complete combustion during the chemical analysis; the latter term means the waste matter produced industrially, and consists, if weighed dry, of the true ash, plus any unburnt carbon. The calculations are therefore as follows:

		Lbs.
Ash in 2240 pounds of coal = 2240×0.12	=	268.8
Ashes corresponding = $268.8 \div 0.80$ (the ashes are 80 per cent. ash)	=	336.0
Carbon in the ashes	=	67.2
Carbon in the coal = 2240×0.72	=	1612.8
Carbon going into the gas (gasified)	=	1545.6
Carbon in 1 cubic foot of gas = $0.162 \div 16$	=	0.010125
Volume of gas produced per 2240 pounds of coal = $1545.6 \div 0.010125$	=	152,652 cu. ft

It will be noted that these calculations absolutely require the percentage of *total* carbon in the fuel, as determined by chemical analysis. This is not a difficult analysis, as it consists in burning the carbon in a heated tube in a stream of oxygen or air free from carbon dioxide; the products of combustion are dried and then passed through caustic potash solution to absorb CO^2 gas, the weight of which is obtained by the increased weight of the potash bulb, and the total carbon thus obtained. The fixed carbon and volatile matter of the coal, as determined by the ordinary proximate analysis, cannot be used in this calculation, since while all the fixed carbon is carbon, the volatile matter is of variable composition, containing such varying proportions of carbon that no fixed percentage of the latter in it can be assumed without considerable possible error.

The calorific power of the gas, per cubic meter or cubic foot, can be calculated from its analysis, using the calorific powers of the combustible constituents as already given in our

tables. This, multiplied by the volume of gas produced per unit of coal, gives the calorific power of the gas as compared with that of the coal from which it is made. The difference is the heat loss in the operation of producing the gas, including loss by unburnt carbon in the ashes. In fact, we may state that the heat balance is based on the following equations:

Heating power of the coal, per unit
—Heating power of the gas per unit of coal
=Calorific losses in conversion.

The latter item is composed of:

Loss by unburnt carbon in the ashes.
Sensible heat of the hot gases issuing.
Heat conducted to the ground.
Heat radiated to the air.

These items may be modified as follows: If the air used is hotter than the normal outside temperature, its sensible heat above this datum should be added to the heating power of the coal, because it increases the total available heat. If the ashes are removed hot, and not allowed to be completely cooled by the incoming air, their sensible heat should be included in the calorific losses during conversion. If the air used is moist, its moisture will be decomposed to hydrogen and oxygen, but the heat absorbed in doing this is exactly represented by the calorific power of this increased amount of hydrogen in the gases, and the heat absorbed is not lost but really represents so much saved as available calorific power of the gases. This item must, therefore, *not* be counted as one of the heat losses during the operation, as those losses have been defined by us. If the fuel is wet, considerable heat is required to evaporate the moisture in it, but this heat is *not* to be reckoned as one of the losses in conversion, if we have taken as the heating power of the coal the practical metallurgical value; that is, its value assuming all the water in its products of combustion to remain as vapor and none to condense. If this value has been so taken, the heat required to vaporize the moisture in the coal will have already been allowed for. Similarly, it may take a little heat energy to break up a bituminous coal so as to expel its volatile matter, but this should not be reckoned in as

a heat loss in the producer, because a little reflection will show that, whatever this amount may be, it has been properly allowed for in the determination or calculation of the total calorific power of the fuel. Jüptner and Toldt call this the "gasifying heat," and use it in all their calculations, but it is doubtful whether it really amounts to an appreciable quantity, for one thing, and even if it does it should not be reckoned as a heat loss in the producer.

Problem 16.

Jüptner and Toldt ran a gas producer with lignite of the following composition: (*Generatoren*, p. 49).

Carbon	69.83	per cent.
Hydrogen	4.33	"
Nitrogen	0.50	"
Oxygen	12.38	"
Moisture	7.25	"
Ash	5.71	"

Of this coal, 3214 kilograms was used in 8 hours, 50 minutes, producing gas which contained, analyzed dry, by volume:

Carbon dioxide, CO^2	5.21	per cent.
Carbon monoxide, CO	23.99	"
Oxygen, O^2	0.63	"
Methane, CH^4	0.25	"
Hydrogen, H^2	10.64	"
Nitrogen, N^2	59.28	"

The ashes produced weighed 22.23 kilograms per 100 kilograms of coal used, and contained 68.76 per cent. of unburned carbon. The calorific power of the coal, determined in the calorimetric bomb (in compressed oxygen, moisture resulting condensed) was 6949 Calories per kilogr. Temperature of hot gases, 282° C.; temperature of air used, 9° C.; humidity, 62 per cent.; barometer, 712 millimeters of mercury.

Required:

1. The volume of gas, measured at 0° and 760 mm. pressure (and assumed dry), produced per metric ton (1000 kilos. = 2204 pounds) of fuel used.

2. The calorific power of the coal, per kilogram, with moisture formed by its combustion assumed uncondensed.

3. The proportion of the calorific power of the coal developable by burning the gas produced from it.

4. The loss of heat in conversion.

5. The loss of heat by unburnt carbon in the ashes.

6. The loss of heat as sensible heat in the gases.

7. The loss of heat by radiation and conduction, expressed:

(*a*) Per unit of coal burnt.

(*b*) Per minute.

8. The volume of air required by the producer, at the conditions of the atmosphere, per kilogram of coal burnt.

Solution:

(1) The gas contains, per cubic meter at standard conditions:

Carbon in CO^2 0.0521×0.54 kilos.
Carbon in CO 0.2399×0.54 "
Carbon in CH^4 0.0025×0.54 "

Total $0.2945 \times 0.54 = 0.1590$ kilos.

The carbon gasified from 1000 kilograms of coal is:

Carbon in coal	= 698.3 kilos.
Carbon in ashes 222.3×0.6876	= 152.8 "
Carbon gasified	= 545.5 "

Therefore,

$$\text{Gas (dry) produced} = \frac{545.5}{0.1590} = 3430 \text{ cubic meters.} \quad (1)$$

(2) The calorific power of the coal as given must be diminished by the heat required to vaporize all the moisture formed by its combustion, leaving such moisture as theoretical moisture at 0° C. There will be formed per kilogram of coal:

From moisture of coal	= 0.0725 kilos.
From hydrogen 0.0433×9	= 0.3897 "
Total	= 0.4622 "

To evaporate this to theoretical moisture at zero (thus

putting the water vapor on the same footing as the other products of combustion, CO^2 and N^2) requires:

$$0.4622 \times 606.5 \text{ (Regnault)}, = 280 \text{ Calories},$$

leaving as the metallurgical or practical calorific power

$$6949—280 = 6669 \text{ Calories}, \qquad (2)$$

(3) The calorific power of each cubic meter of gas (measured dry at standard conditions) is

$$\begin{aligned} CO &= 0.2399\ m^3 \times 3{,}062 = 734.6 \text{ Calories} \\ CH^4 &= 0.0025\ m^3 \times 8{,}598 = 21.5 \quad " \\ H^2 &= 0.1064\ m^3 \times 2{,}613 = 278.0 \quad " \\ &\text{Total} = 1034.1 \quad " \end{aligned}$$

Calorific power of gas from 1 kilogram of coal:

$$1034.1 \times 3.43 = 3547.0 \text{ Calories.}$$

$$\text{which equals } \frac{3547.0}{6669.0} = 53.2 \text{ per cent.} \qquad (3)$$

(4) The loss of calorific power in conversion is 100—53.2 = 46.8 per cent. of the calorific power of the coal, or per kilogram of coal:

$$6669—3547 = 3122 \text{ Calories.} \qquad (4)$$

(5)

$$\text{Carbon in ashes} = 0.1528 \times 8100 = 1237.7 \text{ Cal.}$$
$$= 18.6 \text{ per cent.} \qquad (5)$$

(6) The gases produced carry off, per cubic meter measured dry, the following amounts of heat:

Volume × mean specific heat (0°—282°) = heat capacity per 1°.

$$\begin{aligned} CO^2 \quad & 0.0521 \times 0.432 = 0.0225 \\ CH^4 \quad & 0.0025 \times 0.428 = 0.0011 \\ \left.\begin{matrix} CO \\ O^2 \\ H^2 \\ N^2 \end{matrix}\right\} \quad & 0.9454 \times 0.311 = 0.2940 \\ & \text{Sum} = 0.3176 \end{aligned}$$

Heat carried out = $0.3176 \times 282 = 89.56$ Calories.

Per kilogram of coal = $89.56 \times 3.43 = 307$ Calories.

$$\text{Proportion of calorific power} = \frac{307}{6669} = 4.6 \text{ per cent.}$$

The above result is, however, subject to a small correction, because some of the moisture in the coal goes undecomposed into the gases, and is not represented in the analysis of the dried gas. The amount of this moisture can be obtained with sufficient accuracy by finding how much moisture would be obtained by burning the dried gas from 1 kilogram of coal, and comparing this with the moisture which would be obtained from 1 kilogram of coal itself; the difference must represent the moisture accompanying the gas as water vapor, and which has not been included in the above computation.

Burning 1 cubic meter of gas, the H^2O vapor is:

From CH^4 0.0025×2	= 0.0050	cubic meters.
From H^2 0.1064×1	= 0.1064	" "
	0.1114	" "
Per kilo. of coal = 0.1114×3.43	= 0.3821	" "

But the weight of water vapor from burning 1 kilogram of coal has already been found to be (2) 0.4622 kilograms, the volume of which is

$$0.4622 \div 0.81 = 0.5706 \text{ cubic meters.}$$

Leaving, therefore, 0.5706—0.3821 = 0.1885 cubic meters of water vapor as such accompanying the 3.43 cubic meters of (dried) gas from 1 kilogram of coal. This would take out

$$0.1885 \times 0.382 \times 282 = 20.3 \text{ Calories.}$$

Thus increasing the sensible heat in the gases to

$$307 + 20.3 = 327.3 \text{ Calories} = 4.9 \text{ per cent.} \qquad (6)$$

[In reality, a still further correction should be made; viz.: to add in the moisture in the air used, because it would also reappear as moisture on final combustion of the gases. Its amount is found from the amount of air used, which, if 62 per cent. saturated at 9° would carry moisture having 0.62×8.6 mm. (if saturated) = 5.3 millimeters tension, which represents, barometer being 712 mm., 0.7 per cent, of the volume of the air used, or practically 0.9 per cent. of the volume of nitrogen in the air. Since the nitrogen in the gas represents almost entirely the nitrogen in the air used, the moisture to be accounted for from the air amounts to $0.5928 \times 0.009 = 0.0053$

cubic meters per cubic meter of gas, or = 0.0182 cubic meters per kilogram of coal burnt. This correction is altogether too small to affect the results in this case, but should be taken into account whenever the air used is warm and moist.]

(7) The calorific loss in conversion was 3122 Calories. Of this we have accounted for:

Lost by unburnt carbon in ashes	1237.7	Calories.
Sensible heat of gases (including moisture)	327.3	"
Total	1565.0	"
Loss by radiation and conduction =	1557.0	" (a)

Per 8 hours 5 minutes there is burnt 3214 kilograms of fuel, making the loss of heat by radiation and conduction per minute =

$$\frac{1557 \times 3214}{530} = 9{,}442 \text{ Calories.} \qquad \text{(b)}$$

(8) At the conditions given, each cubic meter of moist air used contained 0.7 per cent. of its volume of moisture, making its percentage composition by volume:

	Water vapor	0.70	per cent.
Air	Oxygen	20.65	"
	Nitrogen	78.65	"

The volume of gas produced per kilogram of coal is 3.43 cubic meters, of which 59.28 per cent. is nitrogen, equal to 2.0333 cubic meters, and weighing $2.0333 \times 1.26 = 2.562$ kilograms. Of this 0.0050 kilograms came from the coal itself, leaving 2.512 kilograms to come from the air, or $2.512 \div 1.26 = 1.9921$ cubic meters. This would correspond to $1.9921 \div 0.7865 = 2.5329$ cubic meters of moist air if measured at standard conditions. At 9° and 712 mm. pressure the real volume of moist air used at prevailing conditions, per kilogram of coal burnt, is

$$2.5329 \times \frac{273+9}{273} \times \frac{760}{712} = 2.80 \text{ cubic meters.} \qquad \text{(8)}$$

It must not be thought that the conditions of working in the above producer represent good practice; they are very poor practice as far as concerns the utilization of the fuel. Many producers make gas having 75 to 90 per cent. of the

calorific power of the coal from which it is made, so that the losses by unburnt carbon and radiation and conduction in this case must be regarded as highly abnormal and very poor practice. The writer chose this example for calculating, because of the carefulness with which Jüptner and Toldt had collected the necessary data, and because it illustrated so well the principles to be employed in similar calculations.

Problem 17.

A gas producer run in Sweden uses saw-dust of the following composition:

Water	27.0 per cent.
Ash	0.5 "
Carbon	37.0 "
Hydrogen	4.4 "
Oxygen	30.6 "
Nitrogen	0.5 "

Assume that it is run by dry air and that 0.5 per cent. of ashes are made. The gas formed, dried before analysis, contains, by volume:

Carbon dioxide, CO^2	6.0 per cent.
Carbon monoxide, CO	29.8 "
Ethylene, C^2H^4	0.3 "
Methane, CH^4	6.9 "
Hydrogen, H^2	6.5 "
Nitrogen, N^2	50.5 "

The gas actually produced is partly dried before use by having its temperature reduced by cold water, in a surface condenser, to 29° C., in order to increase its calorific intensity of combustion.

Required:

(1) The proportion of the moisture in the moist gas which is condensed out.

(2) The calorific intensity of the moist gas, if burned preheated to 800° C. by the theoretical quantity of air preheated also to 800° C.

(3) The calorific intensity of the dried gas, burnt under exactly similar conditions.

Solution:

(1) It is first necessary to find the weight or volume of water vapor accompanying the gas before condensation, next that accompanying it after passing the condenser. The first can be calculated best on the basis of the hydrogen present in the fuel and in the (dried) gas made from it; the difference is the hydrogen of the moisture removed before analysis, *i.e.*, the hydrogen of the moisture in the wet gas.

The first step is to find the volume of gas (dry) produced per unit of fuel, as follows:

Carbon in 1 kilo. of fuel = 0.370 kilos.

Carbon in 1 m^3 of gas = $CO^2+CO+CH^4+2C^2H^4$ $(0.060+0.298+0.069+0.006)\times 0.54$ = 0.2338 "

$$\text{Dry gas per kilo. of fuel} = \frac{0.370}{0.2338} = 1.5825 \text{ m}^3$$

The next step is to calculate the water which would be formed by the combustion of 1 kilogram of fuel:

Water present in fuel.....0.270 kilos.
Water produced by hydrogen.....0.396 "
Total = 0.666 "

$$\text{Volume at standard conditions} = \frac{0.666}{0.810} = 0.8222 \text{ m}^3$$

From this we subtract the moisture which would be produced by the combustion of the 1.5825 cubic meters of dry gas, obtained as follows:

Water from ethylene = $0.003\times 2\times 1.5825$ m^3
Water from methane = $0.069\times 2\times 1.5825$
Water from hydrogen = $0.065\times 1\times 1.5825$
$= 0.209 \times 1.5825 = 0.3307$ m^3

Difference = water vapor to 1.5825 m^3 of dried gas
= 0.8222—0.3307 = 0.4915 m^3
= $0.4915 \div 1.5825$ = 0.3106 m^3 per 1 m^3

of dried gas, as analyzed

This is to be compared with the amount of moisture accompanying the same quantity of (dried) gas as it escapes from the condenser. This is obtained directly from the fact that the gas escaping will be saturated with moisture at 29° C., that the latter will, therefore, have a tension of 30 millimeters (tables), and that, assuming the barometer normal (760 mm.), the partial tensions of moisture and gas proper are as 30 to 760—30, or as 30 to 730. Since their respective volumes (if both were measured separately at normal pressures) are in the same proportion, it follows that each cubic meter of (dry) gas is accompanied by $30 \div 730 = 0.0411$ cubic meters of uncondensed moisture.

The respective quantities of moisture accompanying 1 cubic meter of dry, uncondensable gas, are, therefore, 0.3106 before cooling and 0.0411 after cooling, showing that 13.2 per cent. of all the moisture escapes condensation, and that, therefore,

86.8 per cent. of moisture is condensed. (1)

(2) The wet gas has a calorific power, calculating on the basis of 1 cubic meter of dried gas analyzed:

CO	0.298 ×	3,062 =	912.5	Calories.
C^2H^4	0.003 ×	14,480 =	43.4	"
CH^4	0.069 ×	8,598 =	593.3	"
H^2	0.065 ×	2,613 =	169.8	"
		Total =	1719.0	"

There is added to this available heat, when burned, the sensible heat in the gas itself, at 800° C., and also that of the necessary air, also at 800°.

Heat in gas:

CO,H^2,N^2 =	0.868	$m^3 \times 0.3246$ =	0.2817	Cals. per 1°
CO^2 =	0.060	$m^3 \times 0.5460$ =	0.0328	"
CH^4 =	0.069	$m^3 \times 0.4485$ =	0.0309	"
C^2H^4 =	0.003	$m^3 \times 0.50$ =	0.0015	"
H^2O =	0.3106	$m^3 \times 0.460$ =	0.1429	"
		Calorific Capacity =	0.4898	"

Total sensible heat = $0.4898 \times 800 = 391.8$ Calories.

The air required theoretically is:

For CO $0.298\ m^3 = 0.1490\ m^3$ oxygen
For C^2H^4 $0.003\ m^3 = 0.0090\ m^3$ "
For CH^4 $0.069\ m^3 = 0.1380\ m^3$ "
For H^2 $0.065\ m^3 = 0.0325\ m^3$ "
Sum $= 0.3285\ m^3$ "
$= 1.58\ m^3$ air

Heat in this at $800° = 1.58 \times 0.3246 \times 800 = 410.3$ Calories.

Sum total of heat going into the products:

Developed by combustion.....	1719.0 Cals.
Sensible heat in gas.....	391.8 "
Sensible heat in air.....	410.3 "
Total.....	2520.0 "

The products of the combustion are CO^2, H^2O and N^2, as follows: $CO^2 = 0.060$ (in gas) $+ 0.298$ (from CO) $+ 0.006$ (from C^2H^4) $+ 0.069$ (from CH^4) $= 0.433\ m^3$.

$H^2O = 0.311$ (with gas) $+ 0.006$ (from C^2H^4) $+ 0.138$ (from CH^4) $+ 0.065$ (from H^2) $= 0.520\ m^3$.

$N^2 = 0.505$ (in gas) $+ [1.58 - 0.33 = 1.25]$ (from air) $= 1.755\ m^3$.

Since the 2520.0 Calories remains as sensible heat in the above products, at some temperature t, we have

Heat capacity of the CO^2 $= 0.433\ (0.37 + 0.00022t)$
Heat capacity of the H^2O $= 0.520\ (0.34 + 0.00015t)$
Heat capacity of the N^2 $= 1.755\ (0.303 + 0.000027t)$
Heat capacity of the products $= 0.8688 + 0.00022065t$

and the calorific intensity t must be

$$t = \frac{2520.0}{0.8688 + 0.00022065t}$$

whence

$$t = 1942°. \qquad (2)$$

(3) When the dried gas is burned under similar conditions, the only difference is that $0.2695\ m^3$ of water vapor are absent from the gas and from the products, having been condensed.

This reduces the available heat by the sensible heat in this much water vapor at 800°, viz.:

$$0.2695 \times 0.460 \times 800 = 99.2 \text{ Calories},$$

and decreases the calorific capacity of the products by

$$0.2695\ (0.34 + 0.00015t).$$

Our equation, therefore, becomes

$$t = \frac{2360.2}{0.7772 + 0.00018023t}$$

whence

$$t = 2056°$$

The increased efficiency of the dried gas for obtaining high temperatures is too evident to need further comment, the difference being in round numbers 150° C., equal to 270° F., in favor of the dried gas.

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2. Mixed Gas Producers.

This class of producers are those most commonly used. In them a moderate amount of steam or vapor of water passes with the air into the fire, and is decomposed, producing carbon monoxide and hydrogen gases by the reaction:

$$\underset{18}{\overset{I}{H^2O}} + \underset{12}{C} = \underset{28}{\overset{I}{CO}} + \underset{2}{\overset{I}{H^2}}$$

which may be read as follows: One volume of steam forms one volume of carbon monoxide and one volume of hydrogen; or eighteen parts by weight of water vapor act upon twelve parts of solid carbon, producing twenty-eight parts of carbon monoxide and two parts of hydrogen. If we speak of kilograms as the above weights, then we can call each " volume " spoken of 22.22 cubic meters: or if we call the weights ounces avoirdupois, each " volume " represents 22.22 cubic feet.

The water vapor is admitted either automatically, as in the old Siemen's type of producer, where water was run into the ash pit to be evaporated by the heat radiated from the grate or by hot ashes falling into it, or as in the modern water-seal

bottom producer, where the ashes rest upon water in a large pan, and so are continually kept soaked by capillary action; or, finally, steam is positively blown under the grate, either as a simple steam jet, or, more economically, by using it in a steam blower, so as to have it produce by injector action an air blast sufficient to run the producer. In the latter case the proportions of air and steam may be regulated with precision, and the blast action produced makes the production and delivery of the gas practically independent of chimney draft. The use of steam also rots or disintegrates the ashes, preventing or breaking up masses of clinker, and so facilitating the removal of the ashes.

Steam or water vapor cools down the fire in the producer so that it runs cooler; at the same time gas is produced which is rich in hydrogen, and, therefore, of higher calorific power. This saves unnecessary waste of heat in the producer, and increases the efficiency of the gas in the furnace in which it is burnt. The scientific reasons for these facts are to be found in a consideration of the thermochemistry of the reaction by which steam is decomposed.

$$H^2O + C = CO + H^2$$
$$-69{,}000 \quad +29{,}160 \quad = -39{,}840 \text{ Calories.}$$

This would be the deficit in decomposing 18 kilograms of water if it starts in the liquid state. If, however, it is used as steam at 100° C., each kilogram contains 637 Calories of sensible heat, making $18 \times 637 = 11{,}466$ Calories altogether, leaving the deficit 28,374 Calories, or the deficit

= 1,576 Calories per kilogram of steam decomposed.
= 2,364 Calories per kilogram of carbon thus burnt.

In making this calculation it might be objected that the steam used is often at three or four atmospheres pressure, and its temperature, therefore, over 100° C.; but it must not be overlooked that this steam expands suddenly to atmospheric tension, and that in so doing it cools itself to an amount roughly proportional to its excess pressure so that the expanded steam at atmospheric pressure is usually close to 100° C. When mixed with air, the temperature of the mixture is usually below 100°, some 40° to 50° C., and in this condition some of

the steam is possibly condensed to fog, but it must not be forgotten that the heat of condensation thus given out has been absorbed in raising the temperature of the admixed air, and therefore goes as sensible heat into the bed of burning fuel. For the purpose of calculation, we will, therefore, be very nearly right in assuming that we are dealing in each case with steam at 100° C., requiring the above calculated deficits to be made up, in order for the decomposition to proceed.

It will be evident that any heat thus used in the producer must be sensible heat of the hot carbon, which, if not so used, would be lost as sensible heat in the gases produced or radiated and conducted away from the producer. The basic process of the running of the producer is the burning of carbon to carbon monoxide, liberating 2,430 Calories per kilogram of carbon, which is $2,430 \div 8,100 = 30$ per cent. exactly of the calorific power of the carbon. This heat, if no water vapor gets into the producer, is lost as sensible heat of the hot gases and by radiation and conduction, and is thus largely a dead loss. In Problem 16, for instance, these items figured out 28.25 per cent. of the calorific power of the coal used. Now, the facts are, that while small producers need that much heat to keep them up to working temperature, large producers need very much less, and run far too hot if no steam is admitted to check the rise of temperature. In the largest producers the sensible heat in the gases, plus the losses by radiation and conduction, does not exceed 10 per cent. of the calorific power of the fuel. Out of the 30 per cent. of the calorific power of the carbon inevitably generated, only some 10 per cent. is, therefore, needed to supply the losses in a large producer, leaving 20 per cent. applicable to decomposing steam. We therefore have:

Per 1 Kilo. of Carbon Gasified.

Heat generated	2,430 Calories.
Necessary loss in a large producer	810 "
Useful for decomposing steam	1,620 "
Required to decompose 1 kilo, steam at 212° F.	
$(69,000—11,466) \div 18 =$	3,196 "

Maximum steam decomposable $1,620 \div 3,196 = 0.507$ kilo.

Calculation, therefore, shows that about one-half of a unit weight of steam is the maximum which can be used per unit

weight of carbon burnt to carbon monoxide, consistent with keeping the producer at proper working temperature. This would be equal to

0.088 kilos. of steam per kilo. of air used.
0.088 pounds of steam per pound of air used.
0.114 kilos. of steam per cubic meter of air used.
0.007 pounds of steam per cubic foot of air used.

The above discussion is on the assumption that the bed of fuel in the producer is thick enough, and its temperature always high enough, to burn all the carbon to carbon monoxide. Such is only an ideal condition, for the irregular charging, descent and working of the fuel always allow of some carbon dioxide being produced, and the best regular gas usually contains 1 to 5 per cent. of dioxide, representing some 3 to 20 per cent. of the total carbon oxidized in the producer.

Assuming that on an average 10 per cent. of the carbon oxidized inevitably forms carbon dioxide, we can calculate under these more usual conditions how much steam can be used, because for each kilogram of carbon oxidized, 0.1 kilo. then gives us 8,100 Calories per kilogram instead of 2,430 in the producer, a surplus of

$$0.1 \times (8{,}100 - 2{,}430) = 567 \text{ Calories.}$$

over the conditions when only monoxide is formed. Instead of the 1,620 Calories available for decomposing steam we will now have 2,187 Calories, which will decompose

$$\frac{2{,}187}{3{,}196} = 0.684 \text{ kilo. of steam.}$$

which reckoned on the air used would be

0.108 kilos. of steam per kilo. of air used.
0.108 pounds of steam per pound of air used.
0.140 kilos. of steam per cubic meter of air used.
0.009 pounds of steam per cubic foot of air used.

The above proportions are those which cannot practically be exceeded, if producing gas as low as is usually possible in carbon dioxide.

[Working the producer comparatively cold, with excess of

steam, much larger proportions of carbon dioxide are formed and correspondingly larger proportions of steam are decomposed, but this manner of working is abnormal, is not unusual, and will be discussed under the next heading, treating of Mond gas.]

Making gas containing any given proportion of CO^2 to CO, by volume, the ratio thus obtained is identical with the proportionate weight of carbon oxidized to CO^2 and CO in the producer, and by the application of the principles just described it can be calculated how much steam can be used per unit of carbon oxidized, making proper allowance for losses by radiation, etc.

Illustration: A Siemen's producer with chimney draft produced gas containing, by volume, 4.3 per cent. CO^2 and 25.6 per cent. CO. How much steam could be used per pound of air used, assuming 50 per cent. of the heat generated by the oxidation of the carbon to be needed to run the producer?

Solution:

$$\text{Per cent. of carbon burnt to } CO^2 = \frac{4.3}{4.3+25.6} = 14.4 \text{ per cent.}$$

Heat generated by C to CO^2	$= 0.144 \times 8{,}100$	= 1,166 lb. Cal.
Heat generated by C to CO	$= 0.856 \times 2{,}430$	= 2,080 "
Heat generated per kilo. of C		= 3,246 "
Heat lost by radiation, etc. (50 per cent.)		= 1,623 "
Heat available for decomposing steam		= 1,623 "

$$\text{Steam decomposable} = \frac{1{,}623}{3{,}196} = 0.508 \text{ pounds.}$$

The above is expressed per kilogram of carbon oxidized, but the same proportion is true per pound. The air required per pound of carbon oxidized is found from the oxygen required to form CO and CO^2:

Oxygen for C to $CO^2 = 0.144 \times 8\text{-}3$	= 0.384 lbs.
Oxygen for C to $CO = 0.856 \times 4\text{-}3$	= 1.141 "
	Total = 1.525 "
	Air = 6.608 "
$\text{Volume of air} = \frac{6.608}{0.0808}$	= 81.8 cu. feet.

Steam per cubic foot of air $= \frac{0.508}{81.8}$ = 0.006 lbs.

Steam per pound of air $= \frac{0.508}{6.608}$ = 0.077 "

Air required per pound of steam = 13.0 "

It should easily be seen that whatever heat is absorbed in the producer in decomposing steam, is entirely recovered when the hydrogen thus produced is burnt and steam is reproduced. If then, in any case, it is possible to absorb in the producer, in the decomposition of steam, an amount of heat equal to say, 20 per cent. of the total calorific power of the fuel, then that 20 per cent. is regained and capable of being utilized when the hydrogen so produced is burnt in the furnace. In other words, 20 per cent. *less* of the calorific power of the fuel will be lost in the process of conversion into gas in the producer, and 20 per cent. *more* will be obtained in the burning of the gas when it is used. The great advantages of using steam judiciously are thus clearly evident.

Problem 18.

R. W. Hunt & Co. report the following tests made of the running of a Morgan continuous gas producer. Coal used, " New Kentucky " Illinois coal, run of mine. Composition:

Fixed carbon	50.87	per cent.
Volatile matter	37.32	"
Moisture	5.08	"
Ash	6.73	"
	100.00	"

The ultimate composition was:

Total carbon	69.72	"
Hydrogen	5.60	"
Nitrogen	2.00	"
Total sulphur	0.94	"
Oxygen	11.00	"
Moisture	5.08	"
Inorganic residue (less sulphur)	6.66	"

The ash, on combustion, contains 1.12 per cent. of its weight

of sulphur (as FeS); the ashes obtained from the producer contain 4.66 per cent. of unburnt carbon.

The gas produced, dried, contained by volume:

Carbon monoxide (CO)	24.5	per cent.
Marsh gas (CH^4)	3.6	"
Ethylene (C^2H^4)	3.2	"
Carbon dioxide (CO^2)	3.7	"
Hydrogen (H^2)	17.8	"
Oxygen (O^2)	0.4	"
Nitrogen (N^2) (by difference)	46.8	"

[The moisture and sulphur compounds in the gas not having been determined, we can calculate the former, and, for the purposes of calculation, are justified in assuming the sulphur present in the gas as H^2S, and in subtracting it from the hydrogen. We will also assume that the moisture in the coal goes unchanged into the gases as moisture, and that all the steam used is decomposed. The 0.94 per cent. of sulphur in the coal will furnish 0.86 per cent. to the gases, because $6.73 \times 0.0112 = 0.08$ per cent. will go into the ash as ferrous sulphide. The 0.86 pound of sulphur would produce 0.91 pounds of H^2S, equal in volume to 9.56 cubic feet per 100 pounds of coal used, or (since we will see later that 53.83 cubic feet of gas are produced per pound of coal) there will be 0.2 per cent. of H^2S in the gases, leaving 17.6 per cent. of hydrogen.]

On the basis of above data and assumptions:

Required: (1) The volume of gas produced per pound of fuel used in the producer.

(2) The weight of steam used per 100 cubic feet of air blown in, assuming the air dry.

(3) The proportion of the total heat generated in the producer which is utilized in decomposing steam.

(4) The percentage of increased economy thus obtained reckoned on the calorific power of the fuel.

(5) The efficiency lost by unburnt carbon in the ashes.

(6) The efficiency of the gas, burnt cold, compared with the coal from which it is made.

Solution: (1) Per pound of coal burnt, there remains in the ashes $0.0673 \times (0.0466 \div 0.9534) = 0.0033$ pounds of unburnt carbon, leaving 0.06972—0.0033 = 0.6939 pounds gasified.

One cubic foot of gas, at 32° F., contains the following weight of carbon:

$$\begin{aligned}
\text{C in CO} &= 0.245 \times 0.54 \text{ ounces} \\
\text{C in } CH^4 &= 0.036 \times 0.54 \quad \text{“} \\
\text{C in } C^2H^4 &= 0.032 \times 1.08 \quad \text{“} \\
\text{C in } CO^2 &= 0.037 \times 0.54 \quad \text{“} \\
\text{Total} &= 0.382 \times 0.54 \quad \text{“} \\
&= 0.20628 \text{ ounces av} \\
&= 0.01289 \text{ pounds av.}
\end{aligned}$$

Gas produced, measured dry, per pound of coal, at 32° F.:

$$\frac{0.6939}{0.01289} = 53.83 \text{ cubic feet}$$

(2) If the moisture of the coal is assumed to pass unchanged into the gas, as moisture, then all the hydrogen in the dry gas, in any form or combination, must have come either from hydrogen in the coal or in the air blast. The hydrogen in the coal is given as 5.60 per cent. The hydrogen in the gas is calculated as follows, per cubic foot:

$$\begin{aligned}
H^2 \text{ in } H^2 &= 0.176 \times 0.09 \text{ ounces.} \\
H^2 \text{ in } H^2S &= 0.002 \times 0.09 \quad \text{“} \\
H^2 \text{ in } CH^4 &= 0.036 \times 0.18 \quad \text{“} \\
H^2 \text{ in } C^2H^4 &= 0.032 \times 0.18 \quad \text{“} \\
\text{Total} &= 0.314 \times 0.09 \quad \text{“} \\
&= 0.02826 \text{ ounces av.} \\
&= 0.00177 \text{ pounds av.}
\end{aligned}$$

Hydrogen in gas from 1 pound of coal:

$$0.00177 \times 53.83 = 0.0953 \text{ pounds.}$$

Hydrogen from decomposition of steam:

$$0.0953 - 0.0560 = 0.0393 \text{ pounds.}$$

Weight of steam decomposed per pound of coal used:

$$0.0393 \times 9 = 0.3537 \text{ pounds.}$$

To express this weight relatively to the air blown in, we must calculate the air used per pound of coal, as follows:

Nitrogen in gas per cubic foot

$0.468 \times (14 \times .09) = 0.5897$ oz. av.

$= 0.036856$ lbs. av.

Per pound of coal $= 0.036856 \times 53.83 = 1.9840$ "

Subtract N^2 in 1 pound of coal $= 0.0200$ "

Leaves N^2 from air $= 1.9640$ "

Weight of air $= 1.9640 \times \frac{13}{10} = 2.5532$ "

Volume of air $= 2.5532 \times 16 \div 1.293 = 31.61$ cu. ft.

Steam used per 100 cubic feet of air blown in:

$$= \frac{0.3537}{31.61} \times 100 = 1.119 \text{ pounds.} \qquad (2)$$

(3) The heat utilized in decomposing steam has been found to be 3,196-pound Calories per pound of steam at 212° F. We therefore, have the heat so used per pound of fuel used:

$$0.3537 \times 3{,}196 = 1{,}130\text{-pound Calories.}$$

This quantity must now be compared with the total heat generated in the producer, and the latter quantity can be determinated in two ways: (1) We may subtract from the total calorific power of the coal the calorific power of the gas produced and of the unburnt carbon in the ashes; the difference must be the *net* heat generated in the producer, *i.e.*, the total heat generated minus that absorbed in decomposing steam. The total heat generated is the net heat thus calculated plus the heat absorbed in decomposing steam. (2) We may calculate the heat of formation of the CO and CO^2 in the gas, and assume that as the total heat generated in the producer. This method is not so accurate as (1).

The total calorific power of the coal is given as practically 7,747-pound Calories per pound, water formed being condensed, which would be decreased by the latent heat of vaporization, if the latter is assumed uncondensed. The deduction is $606.5 \times [(0.056 \times 9) + 0.0508] = 337$-pound Calories, leaving 7,410-pound Calories as the practical metallurgical calorific power of the fuel.

Calorific power of the gas (dried) per cubic foot:

CO	0.245 ×	3,062	= 750.2	ounce Cal.
CH^4	0.036 ×	8,598	= 309.5	"
C^2H^4	0.032 ×	14,480	= 463.4	"
H^2	0.176 ×	2,613	= 459.9	"
H^2S	0.002 ×	5,513	= 11.0	"
		Total	= 1994.0	"
			= 124.6	pound Cal.

Calorific power of gas per pound of coal:

$$124.6 \times 53.83 = 6{,}707 \text{ pound Cal.}$$

Calorific power of carbon in ashes:

	$0.0033 \times 8{,}100 = 27$	"
	Sum = 6,734	"
Calorific power of 1 pound coal	= 7,410	"
Net heat lost in conversion	= 676	"
Used in decomposing steam	= 1,130	"
Gross heat generated in producer	= 1,806	"

Proportion of this utilized in decomposing steam:

$$\frac{1{,}130}{1{,}806} = 0.626 = 62.6 \text{ per cent.} \qquad (3)$$

(4) We can state this result in another way, by saying that $1{,}806 \div 7{,}410 = 24.40$ per cent. of the calorific power of the fuel is generated in the producer, of which $1{,}130 \div 7{,}410 = 15.25$ per cent. is utilized to decompose steam, and 9.15 per cent. is lost by radiation, conduction and sensible heat in the gases. The calorific power of the gases represents $6{,}707 \div 7{,}410 = 90.50$ per cent. of the calorific power of the coal of which 15.25 per cent., however, is clear gain from the employment of steam. Reckoning on the total calorific power of the coal, the increased economy from the use of steam is 15.2 per cent. (4)

(5) The loss of calorific power by the unburnt carbon in the ashes is 27-pound Calories, or, on the whole heat available,

$$= \frac{27}{7.410} = 0.36 \text{ per cent.}$$

This loss is exceptionally low, and may be very profitably compared with the analogous loss of 18.6 per cent. occurring in the case discussed in Problem 16.

(6) This has already been calculated as

$$\frac{6,707}{7,410} = 90.50 \text{ per cent.}$$

on the assumption that the gases are burnt cold. If they are burnt hot, say issuing from the producer at 1200° F. (649° C.), and are burnt when at 1,000° F. (548° C.) their sensible heat at 1,000° F. will be added to their efficient heating power, and can be calculated with exactness, using the principle explained and used in requirement (6) of Problem 14. Under such conditions the total efficiency of the producer, reckoned on the calorific power of the coal used, approximates 95 per cent.

To be fair to everybody concerned, however, we must deduct from this the coal required to be burnt to raise the steam used. There is a little over one-third pound of steam used per pound of coal used in the producer. This requires in ordinary boiler practice $\frac{1}{3} \times \frac{1}{8} = \frac{1}{24}$ pound of coal, or about 4 per cent. of the weight of fuel burnt in the producer. The results of the previous calculation must, therefore, be diminished in this proportion, if the steam has to be raised by burning coal under boilers. Under these conditions (6) becomes:

$$90.50 \div 1.04 = 87 \text{ per cent. efficiency.} \qquad (6)$$

If the steam can be obtained from waste gases of a blast furnace, or from the hot producer gases themselves (in case they are going to be burnt cold), then no such deductions need be made. It is very evident, however, that if 9.15 per cent. greater efficiency is gained by burning 4 per cent, more coal to raise the steam, that the net gain would be only 5.15 per cent. Even under these conditions it pays to use steam, because of the greater calorific intensity of the richer gas, the usefulness of the steam for supplying air blast, and the rotting of the clinkers therewith obtained.

3. Mond Gas.

In the Mond producer, an excess of steam is introduced with the heated air used for combustion; the producer is thus run much colder than the ordinary producer, and far more carbon dioxide is present in the gas. In fact, the gas, compared with ordinary producer gas, is very high in carbon dioxide (10 to 20 per cent.), very high in hydrogen (20 to 30 per cent.), very low in carbon monoxide (10 to 15 per cent.), low in nitrogen (40 to 50 per cent.), and carries an extraordinary amount of undecomposed moisture. The fuel used is low-grade bituminous slack, and the object of using so much steam is to keep the temperature in the producer so low that a maximum amount of the nitrogen in the coal is evolved as ammonia. The gas is cooled to ordinary temperature by contact with water spray, so that all but a small amount of moisture is condensed, the ammonia is removed by dilute sulphuric acid, and the cold nearly dry gas is then used for gas engines or in furnaces.

The calorific power of the gas is not low, because the high proportion of hydrogen compensates for the low carbon monoxide, while the great heat evolved by the large formation of carbon dioxide has been mostly absorbed in decomposing steam, and is, therefore, potentially present in the gas in the form of hydrogen.

Problem 19.

Bituminous slack coal used in Mond producers for generating gas for a gas-engine power plant contained:

Moisture	8.60	per cent.
Carbon	62.69	"
Hydrogen	4.57	"
Oxygen	10.89	"
Nitrogen	1.40	"
Ash	10.42	"

Calorific power, determined in a bomb calorimeter, water condensed, 6,786 Calories per unit of dried fuel. Ashes produced 268 pounds per ton (2,240 pounds) of moist slack used; contains 12 per cent. of carbon.

Air used for running is heated to 300° C. by the waste heat of producer gases, and carries in 2½ tons of water as steam (at

same temperature) for every ton of fuel burnt. The steam is generated by a tubular boiler run by the escape gases from the gas engines, but is heated from 100° C. to 300° C. by the waste heat of the producer gases. The latter escape from the producer at 350° C.

Composition of waste gases passing out of condensers at 15° C.:

Carbon monoxide (CO)	11.0	per cent
Hydrogen (H^2)	27.5	"
Marsh gas (CH^4)	2.0	"
Carbonic oxide (CO^2)	16.5	"
Nitrogen (N^2)	41.3	"
Water vapor (H^2O)	1.7	"
	100.0	"

Assume all the nitrogen of the fuel to form ammonia gas NH^3.

Required:

(1) The calorific power of the Mond gas.
(2) The volume of gas produced per ton of fuel used.
(3) The efficiency of the producer.
(4) The weight of steam which is decomposed in the producer.
(5) The proportion of the calorific power of the fuel saved to the gas by the decomposition of steam.
(6) The proportion of the heat generated in the producer which is saved to the gas by the decomposition of steam.
(7) The proportion of the calorific power of the coal lost from the producer by radiation and conduction.

Solution: (1) One cubic foot of the gas at 0° C. would generate the following amounts of heat (water uncondensed).

CO = 0.110 cubic feet × 3062	= 336.8	ounce	Calories.
H^2 = 0.275 cubic feet × 2613	= 718.6	"	"
CH^4 = 0.020 cubic feet × 8598	= 172.0	"	"
Total	= 1227.4	"	"
	= 76.7	pound	"
	= 138.1	B. T. U.	
Per cubic meter	= 1227.4	kilo.	"

If measured at 15° C. (60° F.) the above values will be reduced by the factor $273 \div (273+15)$, and become

Per cubic foot = 72.7 pound Calories.
Per cubic meter = 1163 kilo. " (1)

(2) Carbon in 1 cubic foot of gas at 0° C.:

In CO 0.110×0.54 ounces
In CH^4 0.020×0.54 "
In CO^2 0.165×0.54 "
0.295×0.54 " = 0.1593 ounces
= 0.009956 pounds

Carbon going into gas per pound of fuel burnt:

Carbon in fuel 0.6269 pounds

Carbon in ashes $\frac{268}{2240} \times 0.12 = 0.0144$ "
Carbon in gas = 0.6125 "

Volume of gas (at 0° C.) per pound of fuel used:

$$\frac{0.6125}{0.009956} = 61.52 \text{ cubic feet}$$

Per ton of 2240 pounds = 137,805 cubic feet
At 15° C. (60° F.)

$$= 137{,}805 \times \frac{273+15}{273} = 145{,}375 \text{ " " (2)}$$

(3) The calorific power of the dried fuel is given as 6,786 Calories per pound, water condensed. Since one pound of wet fuel contains 100—8.60 = 91.40 per cent. dried fuel, the calorific power of 1 pound of wet fuel, moisture condensed, is

$6{,}786 \times 0.9140 = 6{,}202$ pound Calories.

But, 1 pound of wet fuel would produce, on combustion,

$0.0860 + 9\ (0.0457) = 0.4973$ pounds moisture,

which, remaining vaporized at 15°, would retain

$0.4973 \times 596 = 296$ Calories,

leaving the net metallurgical calorific power as

6,202—296 = 5,906 Calories.

The 61.52 cubic feet of gas produced per pound of moist fuel will have a calorific power, burnt cold, of

$$61.52 \times 76.7 = 4{,}719 \text{ Calories.}$$

making the efficiency of the producer, on fuel consumed in it,

$$\frac{4{,}719}{5{,}906} = 0.799 = 79.9 \text{ per cent.} \qquad (3)$$

The above figure is true only on the assumption that the steam used is obtained from waste heat, and therefore does not require the combustion of extra fuel

(4) The gas produced contains, per cubic foot, the following amount of hydrogen, free and as CH^4:

As H^2 0.275 cubic feet $\times$ 0.09	= 0.02475	ounces.
As CH^4 0.040 cubic feet $\times$ 0.09	= 0.00360	"
Sum	= 0.02835	"
	= 0.001772	pounds
Per pound moist fuel = 0.001772 $\times$ 61.52	= 0.1090	"
Present as ammonia gas 0.0140 $\times$ (3 $\div$ 14)	= 0.0030	"
Total (not including H as water)	= 0.1120	"
Hydrogen in 1 pound of coal	= 0.0457	"
Hydrogen from decomposition of steam	= 0.0663	"
Water decomposed in the producer	= 0.5967	"(4)

Since the steam introduced weighs 2.5 pounds for every pound of fuel burnt, we see that only

$$\frac{0.5967}{2.5} = 0.2387 = 23.87 \text{ per cent.}$$

of the steam introduced is decomposed.

[In the writer's opinion this unused 76.85 per cent. can only pass in and pass out carrying out sensible heat, and it seems a very wasteful method of keeping down the temperature in the producer. From the standpoint of regarding the 2 pounds of steam as a mere absorber of sensible heat, it could probably be replaced by some of the gases of combustion from the gas engine or open-hearth furnace. The products of combustion of the above gas would contain approximately

Nitrogen	68.7 per cent.
Carbon dioxide	14.7 "
Water vapor	16.6 "

And if the ½ pound of water vapor decomposed in the producer were thus supplied, it would bring in, per pound of coal burnt,

Nitrogen	41.2 cubic feet.
Carbon dioxide	8.8 "
Water vapor	9.9 "

And if the CO^2 thus introduced were reduced to CO, as it probably would be, the gases would receive from this source

Nitrogen	41.2 cubic feet.
Carbon monoxide	27.5 "
Hydrogen	9.9 "

thus producing gas quite up to standard as regards combustibles, while the heat absorbed in the reduction of CO^2 to CO would cool the fire down quite as effectually as the extra steam now used.]

(5) The steam decomposed, 0.5967 pounds per pound of fuel burnt, may be assumed to be at 100° C. on entering the fire, and to therefore absorb 3,196-pound Calories per pound of steam decomposed. The heat absorbed in the producer, and thus transferred into potential calorific power is, therefore

$$3196 \times 0.5967 = 1907 \text{ pound Calories,}$$

which expressed in per cent. of the calorific power of the fuel is

$$\frac{1907}{5906} = 0.323 = 32.3 \text{ per cent} \qquad (5)$$

(6) The heat generated in the producer equals the calorific power of the coal minus the heat lost by carbon in the ashes, minus the calorific power of the gases, plus the heat absorbed in decomposing steam. The loss by carbon in the ashes is

$$\frac{268}{2240} \times 0.12 \times 8100 = 117 \text{ Calories.}$$

The heat generated in the producer is, therefore,

$$5906 - 117 - 4719 + 1850 = 2920 \text{ Calories,}$$

equal to $2920 \div 5906 = 49.4$ per cent. of the calorific power of

the coal. Of this, 1907 Calories is absorbed in decomposing steam, which is $\frac{1907}{2920} = 65.3$ per cent. of the total heat generated. (6)

(7) There are 2922 Calories generated in the producer, of which 1907 are absorbed in decomposing steam, leaving 1015 Calories to supply radiation and conduction and as sensible heat in the hot gases, to which must be added the sensible heat in the hot air and steam used at 300° C.

The air used per pound of coal is found from the nitrogen in the gases:

Nitrogen in 1 cubic foot of producer gas	= 0.413 cubic foot
Nitrogen in 61.52 cubic foot of producer gas	= 25.40 "
Air used = $25.4 \div 0.792$	= 32.08 "
Steam used = $(2.5 \times 16) \div 0.81$	= 49.40 "

Heat in steam and air at 300° C. (from 15° C.):

$32.08 \times 0.3116 \times 285 = 2850$ ounce Calories
$49.40 \times 0.3872 \times 285 = 5450$ " "
Sum = 8300 " "
= 519 pound Calories

Total heat radiated, conducted and in hot gases:

$1015 + 519 = 1534$ Calories.

The heat in the hot gases is as follows, per cubic foot of gas produced:

CO $0.110 \times 0.313 \times 335$ H^2 $0.275 \times 0.313 \times 335$ N^2 $0.413 \times 0.313 \times 335$	=	83.7
CO^2 $0.165 \times 0.450 \times 335$	=	24.9
CH^4 $0.020 \times 0.460 \times 335$	=	3.1
Sum	=	111.7 ounce Calories
	=	7.0 pound Calories.

Per pound of coal burnt:

$7.0 \times 61.52 = 430$ pound Calories

To this must be added the heat in undecomposed water vapor in the gases, as follows:

Steam used per pound of coal	= 2.50	pounds
Steam decomposed per pound of coal	= 0.60	"
Steam remaining in gases	= 1.90	"
Moisture in coal	= 0.086	"
Total in gases	= 1.986	"
Volume = $(1.986 \times 16) \div 0.81$	= 39.2	cubic feet

Heat contained in this at 350° C.:

$$39.2 \times 0.395 \times 335 = 5187 \text{ ounce Calories}$$
$$= 324 \text{ pound Calories}$$

Total heat in producer gases:

$$430 + 324 = 754 \text{ Calories}$$

Heat lost by radiation and conduction:

$$1589 - 754 = 827 \text{ Calories}$$

Proportion of calorific power of coal thus lost:

$$\frac{827}{5906} = 0.140 = 14.0 \text{ per cent.} \qquad (7)$$

When Mond gas is heated in the regenerator of an open-hearth furnace it changes considerably in composition, as is shown by the following analyses made by Mr. J. H. Darby, on gas dried before analysis:

	Before Regenerator.	*After Regenerator.*
Carbonic acid gas, CO^2	17.8	10.5
Carbon monoxide, CO	10.5	21.6
Ethylene, C^2H^4	0.7	0.4
Methane, CH^4	2.6	2.0
Hydrogen, H^2	24.8	17.7
Nitrogen, N^2	43.6	47.8
	100.0	100.0

The above changes are very interesting, and their discussion profitable. Before heating, the gas burns with a non-luminous

flame; after heating, it burns with a brilliant white flame. Let us inquire:

(1) What chemical change occurs during the heating?
(2) What are the relative volumes of the gas before and after heating (excluding water)?
(3) What change in the calorific power is produced by the heating?

(1) An inspection of the analyses shows undoubtedly that at a high temperature the CO^2 cannot hold all its oxygen in the presence of such a large amount of hydrogen, and that the following reaction must occur:

$$\overset{\text{I}}{CO^2} + \overset{\text{I}}{H^2} = \overset{\text{I}}{CO} + \overset{\text{I}}{H^2O}$$

The figures given do not check exactly, but assuming that the above reaction takes place, we can find to what extent, by expressing the composition of the gas after heating for the same amount of *nitrogen* as was in the gas before heating, since this gas is unchanged:

	Before Heating.	*After Heating.*	*Loss or Gain.*
CO^2	17.8	9.6	—8.2
CO	10.5	19.7	+9.2
H^2	24.8	16.1	—8.7
N^2	43.6	43.6	0.0

Since, according to the reaction written, the volume of CO^2 reduced to CO will be equal to the volume of H^2 thus consumed, and will produce an equal volume of CO; the above table proves, within the probable limits of error, that the reaction written actually takes place.

The separation of luminous carbon is probably due to the splitting up of C^2H^4.

The relative volumes of the heated and unheated gases will be inversely as the percentage of nitrogen in each (since this gas is unchanged), viz.: as 47.8 to 43.6, or as 100 to 91.2. The contraction, 8.8 parts, would again correspond almost exactly to the amount of water formed in the assumed reaction, which would be equal to the hydrogen so used, thus giving another check on the validity of the reaction assumed to take place.

The calorific power of 1 cubic foot of original gas is:

CO	0.105× 3,062	=	321.5	ounce Calories
C^2H^4	0.007×14,480	=	101.4	" "
CH^4	0.026× 8,598	=	223.5	" "
H^2	0.248× 2,613	=	648.0	" "
	Sum	=	1294.4	" "
		=	80.9	pound "
Per 100 cubic feet		=	8090	" "

The calorific power of 1 cubic foot of heated gas is:

CO	0.216× 3,062	=	661.4	ounce Calories
C^2H^4	0.004×14,480	=	57.9	" "
CH^4	0.020× 8,598	=	172.0	" "
H^2	0.177× 2,613	=	462.5	" "
	Sum	=	1353.8	" "
		=	84.6	pound "

For 91.2 cubic feet the calorific power would be 84.6×91.2 = 7715 pound Calories.

The net conclusion is that the heated gas (aside from its sensible heat) gives less heat by combustion in the furnace per unit of coal gasified in the producers than the corresponding quantity of unheated gas; but the difference is only some 4 per cent. On the other hand, the calorific power of the heated gas per cubic foot is some 5 per cent. greater than that of the unheated gas, and, therefore, its calorific intensity will have been increased by the heating—quite aside from the question of its temperature being higher, and therefore its sensible heat greater.

4. Water Gas.

This gas is made intermittently, by first burning part of the fuel until the fire is very hot, and then introducing steam, cool or superheated, into the fire. The reaction producing the gas is:

$$\overset{\text{I}}{C} + \overset{\text{I}}{H^2O} = \overset{\text{I}}{CO} + \overset{\text{I}}{H^2}$$

And if the reaction is complete, and only carbon is present as fuel, the gas produced is theoretically composed of equal parts by volume of CO and H^2, the volume of each of these being equal to that of the steam used (if measured at the same temperature and pressure).

Deviations from this ideal composition are caused in practice by the occurrence of undecomposed steam in the gas, also of CO^2 and N^2, which come from the residual gas formed during the heating up of the fire, some of which will get into the first portion of the water-gas produced, and also hydrocarbons, tar and ammonia from the distillation of the fuel. A typical analysis of water-gas, given by Mr. W. E. Case, is:

Hydrogen (H^2)	48.0
Carbon monoxide (CO)	38.0
Methane (CH^4)	2.0
Carbon dioxide (CO^2)	6.0
Nitrogen (N^2)	5.5
Oxygen (O^2)	0.5

The production of water-gas is more expensive than that of other artificial producer gases, because of the large amount of steam necessarily required, the heat lost during the heating up, and the essentially intermittent character of the operation. Its essential advantages are its very high proportion of combustibles, averaging 90 per cent, and the consequent high calorific intensity which it is capable of producing. (Uncarburetted, it is well known that water-gas is a valuable domestic fuel, and illuminant when used in mantle burners; carburetted, it forms our principal illuminating gas, and as such is manufactured on an immense scale. We will treat here only of its metallurgical uses.)

Discussing the manufacture of the gas, the first step is the heating up of the fuel. This is accomplished by blowing air through it. At this point we can distinguish two systems. The older one is that of blowing in air under moderate pressure, which passes through the fire at moderate velocity, and produces a fair grade of ordinary producer gas. This gas is either wasted, or burned in furnaces requiring such quality of gas, or burned in regenerators where heat is stored up to be utilized in the next stage in superheating steam. The newer system is to blow in air at high pressure, such that a large percentage of carbon dioxide remains in the gases, thus nearly completely burning what carbon is oxidized, and storing up a corresponding quantity of heat in the remaining carbon. The incombustible gases produced are passed through a recuperator

or regenerator, where their sensible heat is partly communicated to the steam used, so as to superheat it when forming water-gas. This system consumes the minimum of carbon in " heating up " the fuel, saves time in this unproductive period, and allows the producer to be run longer " on steam." In practice the fuel is probably raised to an average temperature of 1500° C. during the heating up.

We can calculate the efficiency of this heating up, that is, the proportion of the calorific power of the carbon burnt which is stored up in the remaining fuel, if we know how much fuel is in the producer, how much air is blown through, the composition of the gases produced, and the average rise in temperature of the fuel. Since this operation is, however, only supplementary to the real formation of water-gas by the decomposition of steam, we will first make calculations upon the cooling down period, during which water-gas is made.

During the use of steam the reaction absorbs heat, and the producer rapidly cools. Steam is passed through until the temperature of the fuel is 800° C., and must then be stopped, because between 800° and 600° the reaction is mostly

$$C + 2H^2O = CO^2 + 2H^2$$

resulting in a rapid increase of CO^2 in the gas. The heat to decompose steam is furnished partly by the oxidation of carbon to CO, and partly by the sensible heat in the carbon itself. Since the carbon, from temperatures of about 1000° C. up has a specific heat of 0.5, we can easily calculate how much steam can be decomposed before the temperature falls to 800°.

Problem 20.

A Dellwick-Fleischer water-gas producer contains 3 tons of coke (90 per cent. carbon), heated up to 1500° C. Steam, heated to 300° C., is passed through for 8 minutes, until the temperature of the gas escaping is 700° C., or 800° at the fuel bed. The composition of the gas is (Prof. V. B. Lewes):

Hydrogen	50.0
Carbon monoxide	40.0
Carbon dioxide	5.0
Oxygen	1.0
Nitrogen	4.0

Assume 9000 Calories per minute lost by radiation and conduction.

Required: (1) The amount of steam used in the 8 minutes (2) The volume of gas produced in the 8 minutes.

(1) The amount of steam which could have been used is limited by the available heat to decompose it. The latter is furnished by

(*a*) Oxidation of carbon to monoxide.
(*b*) Oxidation of carbon to dioxide.
(*c*) Sensible heat of the carbon and ash of fuel.
(*d*) Sensible heat of the steam used.

While the items of heat absorption and loss are:

(*e*) Decomposition of the steam.
(*f*) Sensible heat in the gases.
(*g*) Radiation and conduction.

The simplest way to arrive at a solution is to make a few necessary assumptions, and to then let X represent the weight of steam used. The assumptions are that the average temperature of the fuel bed falls to 1000° C., that the average temperature of the escaping gases is $(1500+700)\div 2 = 1100°$ C., that the average specific heat of carbon in the range 1000—1500 is 0.5, and of the ash of the fuel 0.25. Then, casting up a heat balance sheet in terms of X, we can finally arrive at an expression for the heat which was available during the 8 minutes for decomposing steam, and thus at the weight of steam decomposed, and (making this equal to X) at a solution.

(*a*) The analysis of the gas shows that eight times as much carbon was burnt to monoxide as to dioxide, making the equation of combustion:

$$9C + 10H^2O = 8CO + CO^2 + 10H^2$$

By weight, $8\times 12 = 96$ parts of carbon was burnt to CO per $10\times 18 = 180$ parts of steam used, or 0.533 parts per one part of steam. The heat generated in forming monoxide is, therefore:

$$0.533\times X\times 2430 = 1296\ X \text{ Calories.}$$

(*b*) Only one-eighth as much carbon burns to dioxide, giving, therefore, as the heat evolved:

$$(0.533\div 8)\times X\times 8100 = 540\ X \text{ Calories.}$$

(*c*) 3000 kilos. of fuel, representing 2700 kilos. of carbon and 300 kilos. of ash, cool from 1500° to 1000°:

$$2700 \times 0.50 \times 500 = 675{,}000 \text{ Calories}$$
$$300 \times 0.25 \times 500 = 37{,}500 \quad \text{“}$$
$$\text{Sum} = 712{,}500 \quad \text{“}$$

(*d*) $X \div 0.81$ will be the volume of the steam used at normal conditions, which brings in considered only as vapor, at 300°:

$$(X \div 0.81) \times 0.385 \times 300 = 142.6\ X \text{ Calories.}$$

The sum total of (a) + (b) + (c) + (d) gives the total available heat, viz.:

$$1978.6\ X + 712{,}500 \text{ Calories.}$$

(*e*) The steam used requires for its decomposition, considered theoretically as cold steam, producing cold products:

$$(X \div 9) \times 29{,}042 = 3227\ X \text{ Calories}$$

(*f*) The gas being 50 per cent. hydrogen, and the latter being equal to the volume of steam used, the volume of gas must be $2 \times (X \div 0.81)$, which multiplied by the mean specific heat of gas of this composition between 0° and 1100° per cubic meter, and by the temperature, will give the heat thus carried out of the producer:

$$2\ (X \div 0.81) \times 0.347 \times 1100 = 942.5\ X \text{ Calories}$$

(*g*) $9000 \times 8 = 72{,}000$ Calories.

The sum total of (e) + (f) + (g) gives the total heat distribution, viz.:

$$4{,}169.5\ X + 72{,}000 \text{ Calories.}$$

Since the heat available equals the heat distributed:

$$1{,}978.6\ X + 712{,}500 = 4{,}169.5\ X + 72{,}000$$

or $$X = 292 \text{ kilograms} \qquad (1)$$

(2) The volume of this steam, at assumed standard conditions, would be

$$292 \div 0.81 = 360 \text{ cubic meters,}$$

and of gas, since it is 50 per cent. hydrogen,

$$360 \times 2 = 720 \text{ cubic meters.}$$

The above figures represent the maximum attainable production, on the assumption that sufficient steam-generating power is available to furnish the steam, and that the fuel in the producer is of small size and the bed so uniform that the production of gas is regular all over it. In practice, figures considerably below this are attained, but it is always well to know the possible maximum which is attainable.

Problem 21.

In a Dellwick-Fleischer water-gas producer the heating up is accomplished in 2 minutes by blast from a Root blower, furnishing air through a 9.5 in h pipe at a total water-gauge pressure of 19 inches of water, temperature of air 15° C. The gases escaping from the producer analyze:

Carbon dioxide	17.9 per cent.
Carbon monoxide	1.8 "
Nitrogen	78.6 "
Oxygen	1.7 "

Temperature of waste gases 900° C.; heat lost by radiation and conduction 9000 Calories per minute; assume producer to contain 3000 kilos. of fuel, consisting of 90 per cent. carbon and 10 per cent. ash.

Required: (1) The average rise in temperature of the fuel bed.

(2) The proportion of the heat generated which is thus stored up as useful heat for producing water-gas.

(3) Assuming that the production of water-gas lasts 8 minutes, during which 2500 Calories are absorbed from the fuel bed per kilogram of steam used, what should be the steam supply in kilograms per minute?

(4) The ratio between the volume of air supplied during the blowing up period and the weight of steam used in the gas-making period.

Solution: (1) We must first find the amount of air furnished by the blower. To do this, we calculate the pressure head in terms of air at 15° C., instead of water, and then apply the well-known formula $V = \sqrt{2g.\,h.}$ Water is 772 times as heavy as air at 0° C., and, therefore, 19 inches of water pressure would represent $19 \times 772 \div 12 = 1222$ feet of air pressure (that is, a column of fluid as light as air, 1222 feet high). But

air at 15° is lighter still than air at 0°, in the ratio 273 to 288, so that the air pressure measured in terms of air at 15° will be

$$1222 \times \frac{288}{273} = 1290 \text{ feet}$$

The velocity of the air supplied will therefore be, in feet per second:

$$V = \sqrt{64 \times 1290}$$

$$= 287 \text{ feet per second,}$$

and the volume delivered, per minute, at 15° C.:

$$287 \times 60 \times (0.7854 \times 9.5 \times 9.5 \div 144) \text{ cubic feet}$$

$$= 17{,}220 \times 0.492 = 8472 \text{ cubic feet,}$$

which in terms of air at 0° C., would be

$$847 \times \frac{273}{288} = 8050 \text{ cubic feet}$$

$$= 228 \text{ cubic meters}$$

The volume of waste gases produced in the 2 minutes can be found from the relative percentages of nitrogen in the air (79.2) and in the gases (78.6), as follows:

$$228 \times 2 \times \frac{79.2}{78.6} = 459.5 \text{ cubic meters}$$

Containing, therefore, from its analysis:

Carbon dioxide	82.25	cubic meters
Carbon monoxide	8.27	" "
Oxygen	7.81	" "
Nitrogen	361.15	" "
	459.48	" "

The carbon burnt to CO^2 and CO will be:

C to CO^2	$82.25 \times 0.54 =$	44.42 kilos.
C to CO	$8.27 \times 0.54 =$	4.47 "
	Sum =	48.89 "

And the heat thus generated:

C to CO^2	$= 44.42 \times 8100 =$	359,800 Calories
C to CO	$= 4.47 \times 2430 =$	10,860 "
	Sum =	370,660 "

To find the amount of this heat left in the producer at the end of the 2 minutes blowing up, we must subtract the $2\times 9000 = 18{,}000$ Calories lost by radiation and conduction, and then, in addition, the heat carried out by the hot gases, at an average temperature of 900° C., which latter will be:

CO, O^2, N^2	$377.25\times 0.327\times 885$	= 109,150 Calories
CO^2	$82.25\times 0.571\times 885$	= 41,565 "
	Sum	= 150,715 "

Heat left in the fuel bed:

$$370{,}660 - 168{,}715 = 201{,}945 \text{ Calories}$$

heat capacity of the fuel bed per 1° C.:

3000×0.9 kilos. carbon	$\times 0.5$	= 1370 Calories
3000×0.1 kilos. ash	$\times 0.25$	= 75 "
	Sum	= 1445 "

Average rise in temperature of the fuel bed.

$$\frac{201{,}945}{1445} = 140° \text{ C.} \qquad (1)$$

(2) The useful heat thus stored up in the fuel bed amounts to the following proportion of the total heat generated during the blowing up:

$$\frac{201{,}945}{370{,}660} = 0.545 = 54.5 \text{ per cent.} \qquad (2)$$

(3) Steam which can be decomposed in the gas-producing period:

$$\frac{201{,}945}{2500} = 80.8 \text{ kilograms}$$

$$= 10.1 \text{ kilograms per minute} \qquad (3)$$

(4) Air supplied in 2 minutes = 456 cubic meters. Steam used in 8 minutes = 80.8 kilograms.

$$\text{Ratio} = \frac{80.8}{456} = 0.177 \text{ kilos. steam per 1 m}^3 \text{ air} \qquad (4)$$

$$= 0.177 \text{ ounce steam per 1 ft}^3 \text{ air}$$

$$= 1.1 \text{ pounds steam per 100 ft}^3 \text{ air}$$

CHAPTER VII.

CHIMNEY DRAFT AND FORCED DRAFT.

In all problems concerning combustion, we must furnish the air needed for combustion either by suction or by pressure. The original and almost universal method is by chimney draft; the more positive and reliable method is forced draft. Often the two are combined with very satisfactory results.

The waste heat from any metallurgical process or furnace is generally considerable. Most furnaces must be kept above a red heat, and the gases pass directly out of the furnace into the chimney. In such cases the chimney is indicated as the proper source of draft, because it utilizes, although very inefficiently, the ascensive force of the hot gases, and thus works by otherwise wasted energy. In other cases it is practicable to pass the gases through boilers before they go to the chimney, and thus to raise large amounts of steam. The gases are then cooled down so far that they enter the chimney too cold to furnish all the draft needed; in such cases a small fraction of the steam generated will run a steam engine or steam turbine, and run a fan capable of furnishing all the draft needed. In this manner considerable steam is available for other purposes, and great economy is effected.

Chimney Draft.

The principles involved are not obscure or complicated. The total pull, or suction, which a chimney can produce, assuming it to be filled with hot air, is simply due to the ascensive force of the hot air inside, and the measure of this is the difference of weight of the chimney full of hot gases and what it would be if filled with cold air of the temperature outside.

Illustration: A chimney is 6 feet square inside and 100 feet high, uniform, with the gases inside at an average temperature of 500° F., and specific gravity (air = 1) of 1.06. The

air outside is at 80° F. What is the ascensive force of the hot gas inside, in total pounds, in ounces per square inch and inches of water gauge?

The volume of the space in the chimney—chimney volume—is $100 \times 6 \times 6 = 3600$ cubic feet. This volume, filled with air at 32° F., would weigh

$$3600 \times 1.293 = 4654.8 \text{ oz. av.} = 290.9 \text{ pounds.}$$

And, filled with gas at 500° F.,

$$290.9 \times 1.06 \times \frac{491}{500-32+491} = 157.9 \text{ pounds.}$$

If filled with outside air, at 80° F., the weight would be

$$290.9 \times \frac{491}{80-32+491} = 265.0 \text{ pounds.}$$

We, therefore, see that the hot gases in the chimney, weighing 157.9 pounds, displace 265.0 pounds of cold air, and the tendency of the former to rise upwards in this ocean of air must be

$$265.0-157.9 = 107.1 \text{ pounds.}$$

To put it in another way, if a piston fitted into the chimney at the bottom, and could move without friction, the piston would have to be loaded with 107.1 pounds to keep it from moving up the chimney. The total upward pull of the chimney is therefore 107.1 pounds.

Since this would be exerted on a piston $6 \times 6 = 36$ square feet in area, the pull or suction per square foot, in pounds, is $107.1 \div 36 = 2.98$ pounds, and in ounces per square inch.

$$(2.98 \div 144) \times 16 = 0.331 \text{ ounce per square inch.}$$

If the pull or suction is measured on a gauge, as by water pressure, the pressure of a 1-foot column of water at ordinary temperatures is 1000 ounces per square foot, or 1 inch of water is

$$(1000 \div 144) \div 12 = 0.597 \text{ ounces per square inch.}$$

The total pull of the chimney is therefore equivalent to

$$\frac{0.331}{0.579} = 0.57 \text{ inch of water gauge.}$$

By exactly similar methods of calculation the theoretical total suction of a chimney of any given height and temperature of gases inside and of air outside may be obtained. The suction expressed in ounces per square inch, or in water gauge is, of course, independent of the cross-sectional area of the chimney; it depends only on its height and on the temperatures inside and outside.

The above calculated total suction (allowing nothing for friction, etc.) is called the total head of the chimney, and is usually expressed in terms of cold air (at 0° C.) instead of in water. Cold air is a fluid, and water is 772 times as heavy as it; therefore, a gauge pressure or hydrostatic head of 0.57 inch of water is the same as

$$0.57 \times 772 = 440 \text{ inches of air.}$$
$$= 36.5 \text{ feet of air.}$$

What this head really represents is clearly seen from the above calculation. Its value is to be obtained directly from the height of the chimney, temperature inside and out and specific gravity of the chimney gases (air = 1) by the following relations, in which

h_0 = total head in feet of air at 32° F.
h_0 = total head in meters of air at 0° C.
t = temperature in the chimney, F°.
t = temperature in the chimney, C°.
t' = temperature of outside air, F°.
t′ = temperature of outside air, C°.
D = Specific gravity of chimney gases, air = 1.
H = Height of chimney in feet.
H = Height of chimney in meters.

$coef$ = coefficient of gaseous expansion, F° $= \frac{1}{491}$

coef = Coefficient of gaseous expansion, C° $= \frac{1}{273} = \alpha$

$$h_0 = H \left[\frac{(1 - D + coef\ [(t - 32) - D\ (t' - 32)]}{[1 + coef\ (t' - 32)]\ [1 + coef\ (t - 32)]} \right]$$

$$\mathrm{h}_0 = \mathrm{H} \left[\frac{(1 - D + \mathrm{coef}\ (t - Dt')}{(1 + \alpha t')\ (1 + \alpha t)} \right]$$

The author is not fond of using formulas whenever their use can be avoided. The above formulas express in the simplest mathematical form the principles which have been so far explained and used in the calculations, but it is strongly urged that the formulas be kept " for exhibition purposes only," and that when any specific case is to be worked it be attacked from the standpoint of the principles involved, as explained in the case worked. In other words, if one understands properly and thoroughly the basic principles, he has no need of the formula; if one does not understand the principles, the formula had better be kept forever in " innocuous desuetude."

The total head, obtained as above, is the theoretical head. It is like the pressure on the piston of a locomotive—the total available force for all purposes. Just as the pressure on the locomotive piston is used up in friction in the engine and in moving the engine itself, and the residue is the *available* pull on the draw-bar which moves the train, so the total head of the chimney is partly used up in friction in the chimney itself, partly in giving velocity to the gases as they pass out of the chimney, and the residue is the *available* head which draws or pulls the gases through fire-grates, furnaces and flues up to the base of the chimney. If the chimney could be momentarily completely closed at the bottom, except for the gauge opening, and the gas inside be brought to rest, the gauge would show the total head; as soon as dampers are opened connecting the flues, gas moves up the chimney, and the gauge pressure is lessened by the head required to move the gases and that absorbed in the friction in the chimney.

Head Represented in Velocity of Issuing Gases.—This item always exists when the chimney is working, and depends only on the velocity of the gases as they escape and their temperature. The hydraulic head necessary to give any fluid a velocity V is simply the same as the height which a falling body must fall in order to acquire that same velocity; *i.e.*:

$$h = \frac{V^2}{2g}$$

in which expression g is the constant acceleration of gravity, 9.8 meters or 32.2 feet, and the velocity is in meters or feet per second. If we know, therefore, the velocity of the gases

issuing from the chimney, or can calculate or assume it, we can get h. In practice the velocity does not vary within very wide limits. In small house chimneys it may not exceed 3 feet per second, in boiler chimneys 6 to 12 feet per second, in furnace chimneys 12 to 20 feet per second. The temperatures of these issuing gases is, moreover

	C°	F°
In small chimneys.....	100 to 200	200 — 350
In boiler chimneys.....	100 to 300	200°— 550
In furnace chimneys.....	300 to 1000	550°—1800°

If the chimney in question has, therefore, a known velocity of exit of its gases, h can be calculated; but it must not be forgotten that h will be in terms of the kind of gases which is escaping; *i.e.*, of hot gas, and to subtract it from or compare it with h_0 we must reduce it to its equivalent head in terms of cold gas. This is merely a matter of taking into account the specific gravities or relative densities of hot gas and cold air, which are inversely proportional to their absolute temperatures; that is, if D represents the relative density of air and chimney gases at the same temperature:

$$h_0{}^{vel.} = h \times \frac{D}{1+\alpha t} = \frac{V^2}{2g} \cdot \frac{D}{1+\alpha t}$$

Illustration: Assuming the actual velocity of the gases issuing from a furnace chimney to be 15 feet per second, and their temperature 500° F., density 1.06 (air = 1), what will be the head represented by the velocity of these gases in terms of cold air at 32° F.?

The head represented, *in terms of hot gases* at 500° *F.*, is

$$h = \frac{V^2}{2g} = \frac{15^2}{64.3} = 3.5 \text{ feet.}$$

In terms of air at 500° F. is

$$3.5 \times 1.06 = 3.71 \text{ feet.}$$

And in terms of air at 32° F.,

$$3.71 \times \frac{491}{500-32+491} = 1.9 \text{ feet.}$$

Out of the total head which this chimney produces (say 36.5 feet), 1.9 feet is represented by the velocity of the issuing gases, or 5.2 per cent. of the whole, leaving 34.6 feet to represent loss by friction in the chimney and the available head. We will proceed to discuss the loss of head due to friction in the chimney.

Head Lost in Friction in the Chimney.—This varies with the smoothness or roughness of the walls, and has been determined experimentally for air moving with different velocities. The manner of expressing the friction loss is, to put it as a function of the head necessary to give the gases their actual velocity, assuming there were no friction. Thus, supposing as in the preceding paragraph, the actual velocity of the hot gases is 15 feet per second, and the head (in terms of cold air) necessary to give that velocity, not considering friction, is 1.9 feet, then the head lost in friction in getting up this velocity will be

$$h^{\text{friction}} = 1.9 \times \frac{H}{d} K.$$

That is, it will be proportional to H, the height of the chimney, inversely as d, the diameter or side, if square, and to a coefficient K, determined by experiment. The latter varies, according to Grashof's experiments, between 0.05 for a smooth interior to 0.12 for a rough one, and averages 0.08.

Illustrations: Assuming the height of the chimney, 100 feet, its section to be 6 feet square, the coefficient of friction K = 0.08, and the head represented by the net velocity of the hot gases in the chimney to be 1.9 feet of cold air, what is the head lost in friction in the chimney?

The ratio of height to side is $100 \div 6 = 16.67$, which multiplied by K gives 1.33 as the value of the function containing these three terms. This means that 1.33 times as much head has been lost in friction as is represented by the net actual velocity of the gases as they pass up the chimney. Therefore,

$$h^{\text{friction}} = 1.9 \times 1.33 = 2.5 \text{ feet cold air.}$$

Another way of looking at this, which is sometimes useful in considering the height of a chimney, is to say

$$h^{\text{friction}} = 0.025\ H.$$

Or, that in this case, the head lost in friction amounts numerically to one-fortieth the height of the chimney.

If we subtract the head lost in friction plus that represented in the net velocity of the gases, from the total gross head, the residue is that available for doing work external to the chimney. In the specific case of the preceding illustrations we have

h_0 = total head	= 36.5 feet	= 100 per cent.
$h^{velocity}$ = velocity head	= 1.9 "	= 5 "
$h^{friction}$ = friction in chimney	= 2.5 "	= 7 "
$h^{available}$ = available head	= 32.1 "	= 88 "

Available Head of a Chimney.—This is the part of the total head which remains after subtracting the head lost in friction in the chimney and that represented by the velocity of the issuing gases. In the specific cases considered in the above illustrations, the net available head amounted to 88 per cent. of the whole theoretical head. If we assume limiting conditions as found in practice, we can find the limiting values of this proportion. Calling the cases I and II, those with minimum and maximum absorption of head in the chimney itself, we have

	Case I.	*Case II.*
Temperature of issuing gases	100° C.	1000° C.
Velocity of issuing gases per second	1 meter	7 meters
Ratio H to d	10	50
Coefficient K	0.05	0.12
Specific gravity of gases (air = 1)	1.00	1.06
Head as velocity of gases (meters of air)	0.04 m.	0.56 m.
Head as velocity of gases (feet of air)	0.13	1.87
Head absorbed in friction (meters of air)	0.02	3.36
Head absorbed in friction (feet of air)	0.07	11.2
Head used up in chimney (meters)	0.06 to	3.92
Head used up in chimney (feet)	0.20 to	13.0
Water gauge pressure thus lost, m.m	0.1 to	5.0
Water gauge pressure thus lost, inches	0.003 to	0.2

The available head, will, therefore, be the theoretical total head minus a loss in the chimney itself, which may amount to a maximum of 3.9 meters or 13 feet, representing an absorption of water gauge pressure up to 5 millimeters, or 0.2

inch at a maximum. Under ordinary conditions half these quantities would be a rather high chimney loss.

In most conditions which confront the metallurgist, the question is to determine how high a chimney should be built in order to supply a certain available draft determined by practice to be necessary. For instance, to burn a certain amount of coal per hour on any grate requires a certain amount of draft. This amount is increased if the draft is increased, and *vice versa*. In boilers, 18 pounds of coal burned per square foot of grate surface per hour is highly economical practice, and requires a draft of 0.4 inch to 0.8 inch of water gauge, according to the kind of coal burned. In furnaces where the amount of coal burned is greater per hour there will be usually a correspondingly greater temperature in the chimney. To calculate the height of chimney required it is necessary to assume only the temperature in the chimney, the available draft required and an average chimney loss.

Problem 22.

It is desired to design a chimney for a puddling furnace, the grate of which is 4 feet by 6 feet, and which shall burn 30 pounds of bituminous coal per hour per square foot of grate surface. Temperature of gases entering the chimney 1200° C., at the top probably 1000° C. Specific gravity of gases 1.03 (air = 1). Draft required 0.6 inch of water gauge. Outside temperature 30° C.

Solution: We can assume that since the gases will be at an average temperature of 1100° C. in the chimney, their velocity will be high, and that at least 0.1 inch of water gauge pressure will be absorbed by the chimney itself. This makes a total requirement of 0.7 inches of water for total head, or

$$h_0 = 0.7 \times 772 \div 12 = 45 \text{ feet of cold air.}$$

Or an unbalanced pressure or ascensive force of

$$45 \times 1.293 \div 16 = 3.64 \text{ pounds per square foot.}$$

Considering the air outside the chimney, its weight at 30° C. is equal, per cubic foot,

$$1.293 \times \frac{273}{303} \div 16 = 0.073 \text{ pounds.}$$

The gases inside the chimney weigh, per cubic foot,

$$1.293 \times 1.03 \times \frac{273}{1100+273} \div 16 = 0.0166 \text{ pounds.}$$

The height of the chimney being called H and its cross-section S, the volume is $H \times S$, and the weight of hot gas inside it is

$$(H \times S) \times 0.0166 \text{ pounds.}$$

And of an equal volume of cold air outside

$$(H \times S) \times 0.073 \text{ pounds,}$$

giving a total ascensive force of

$$(H \times S) \times 0.0564 \text{ pounds.}$$

But there is needed a total ascensive force of

$$S \times 3.64 \text{ pounds,}$$

in order to give the pull of 3.64 pounds per square foot, and, therefore, of necessity,

$$H \times S \times 0.0564 = S \times 3.64,$$

from which

$$H = \frac{3.64}{0.0564} = 64.5 \text{ feet.}$$

Concerning the cross-section of this chimney, it would not be safe to make it less in diameter than one-fiftieth of its height, because of lack of stability; in fact, one-twenty-fifth would be better practice. This consideration would make its internal diameter 2 ft. 7 inches, area 5.2 square feet. Another way of arriving at a diameter is to calculate the volume of the hot gases which must pass up the chimney and assume for them some maximum velocity in the chimney, such as, let us say, 6 meters (20 feet) per second, and so get the minimum area necessary for filling this condition as follows:

Coal burnt per hour $4 \times 6 \times 30$	=	720 pounds.
Air theoretically necessary, assuming average bituminous coal (see Prob. 1) = 123 $\times 720$	=	88,560 cubic feet.

Products of combustion at standard conditions = 129×720 = 92,880 cubic feet

Volume chimney gases at 1100° C. =

$$92{,}880 \times \frac{1100+273}{273} = 467{,}100 \text{ "}$$

Volume per second = 130 "

Area of chimney, if maximum velocity is 20 feet per second = 6.5 sq. feet

Diameter, if round = 2 ft. 10 in.

This chimney would do its work better, and there would be much less loss in friction, if the internal diameter were made 25 per cent. greater than the above calculated minimum, say, therefore, 3 feet 6 inches, making the area nearly 50 per cent. greater and cutting down the velocity in the chimney to 13.5 feet per second.

Problem 23.

In the case of the puddling furnace of Problem 22, assume that the hot gases, instead of going directly into the chimney, are passed through the flues of a boiler placed above the furnace, and thence pass into the chimney at a point 15 feet higher than before. Assume chimney 3 feet 6 inches internal diameter, 64.5 feet high above the furnace flue, and that the gases now passing into it 15 feet higher up are at 350° C., and cool to 250° C. at the top of the chimney. The boiler flues introduce additional frictional resistance equal to 0.1 inch of water. The boiler raises steam at a net efficiency of 45 per cent., the steam engine utilizes the steam at a mechanical efficiency of 20 per cent., and a centrifugal fan supplies the forced draft needed at a mechanical efficiency of 25 per cent.

Required: (1) The total head of the chimney, when the furnace discharged directly into it, and the average temperature of the gases in it was 1100° C., and specific gravity 1.03 (air = 1).

(2) The head absorbed as velocity of the outgoing gases, their temperature being 1000° C.

(3) The head lost in friction in the chimney, in this case.

(4) The head which was available to run the puddling furnace.

(5) The total head of the chimney with the gases entering 15 feet above former flue, and average temperature 300° C.

(6) The head absorbed in this case as velocity of outgoing gases, their temperature being 250° C.

(7) The head lost in friction in the chimney in this case.

(8) The available head to draw gases into the chimney.

(9) The deficit of head which must be made up by forced blast under the grate of puddling furnace.

(10) The horse-power absorbed by the fan which furnishes this blast.

(11) The horse-power furnished by the engine using the steam from the boiler.

(12) The excess of power which is thus saved and available for other purposes.

Solution:

(1) Volume of gases in chimney:

$$64.5 \times 3.5 \times 3.5 \times 0.7854 = 620.5 \text{ cu. ft.}$$

Weight at 32° F. (0° C.):

$$620.5 \times (1.293 \div 16) \times 1.03 = 51.65 \text{ lbs.}$$

Weight if temperature is 1100° C.:

$$51.65 \times \frac{273}{1100+273} = 10.27 \text{ lbs.}$$

Weight of equal volume of air outside at 30° C.:

$$620.5 \times (1.293 \div 16) \times \frac{273}{30+273} = 45.18 \text{ lbs}$$

Difference of weight = ascensive force,

$$45.18 - 10.27 = 34.91 \text{ lbs.}$$

Ascensive force per square foot,

$$34.91 \div 9.62 = 3.63 \text{ lbs.}$$

Total head in terms of cold air at 0° C.,

$$3.63 \div (1.293 \div 16) = 44.9 \text{ ft.} \quad (1)$$

In terms of water gauge pressure,

$$44.9 \times 12 \div 772 = 0.685 \text{ ins.} \quad (1)$$

(2) Volume of gases per hour at 0° C.,
(Prob. 22) = 92,880 cu. ft.

Volume at 1000° C.,

$$= 92{,}880 \times \frac{1000+273}{273} = 433{,}100 \text{ cu. ft.}$$

Velocity per second,
$433{,}100 \div (3600) \div 9.62 = 12.50$ ft.

Head necessary to give this velocity, in terms of hot gases, at 1000° $= (12.50)^2 \div 64.3\ (2g) = 2.43$ ft.

In terms of gases at 0° C.,

$$2.43 \times \frac{273}{1000+273} = 0.52 \text{ ft.}$$

In terms of air at 0° C.,
$0.52 \times 1.03 = 0.55$ ft. (2)

In terms of water gauge pressure,
$0.55 \times 12 \div 772 = 0.008$ in. (2)

(3) Assuming K, the coefficient of friction, 0.08, then

$$h_0 \text{ friction} = \frac{V^2}{2g} \quad \frac{273}{273+t} \quad \frac{H}{d} \text{ K. D.}$$

This is only an abbreviated form of the operations done under (2), adding the terms which account for the height, diameter and friction. Now, the velocity per second:

$$V = 92{,}880 \times \frac{1100+273}{273} \div 3600 \div 9.62 = 13.5 \text{ ft.}$$

Head necessary to give this velocity in terms of air at 0°,

$$(13.5)^2 \div 64.3 \times \frac{273}{273+1100} \times 1.03 = 0.58 \text{ ft.}$$

Proportion of this velocity head lost in friction =

$$\frac{H}{d} \text{ K} = \frac{64.5}{3.5} \times 0.08 = 1.47$$

Head lost in friction in chimney,

$$0.58 \times 1.47 = 0.85 \text{ ft.} \qquad (3)$$

In terms of water gauge pressure,

$$0.85 \times 12 \div 772 = 0.013 \text{ in.} \qquad (3)$$

(4)	*Cold Air.*	*Water Gauge.*	
Total head	44.90 feet	0.685 inch	
Absorbed in velocity of gases	0.55 "	0.008 "	
Absorbed in friction in chimney	0.85 "	0.013 "	
Available for the furnace	43.50 "	0.664 "	(4)

(5) Volume of chimney gases,

$$(64.5—15) \times 3.5 \times 3.5 \times 0.7854 = 475.7 \text{ cu. ft.}$$

Weight at 300° C., specific gravity 1.03 (air = 1).

$$475.7 \times (1.293 \div 16) \times 1.03 \times \frac{273}{273+300} = 18.86 \text{ lbs.}$$

Weight of equal volume of outside air at 30° C.,

$$475.7 \times (1.293 \div 16) \times \frac{273}{273+30} = 34.68 \text{ lbs.}$$

Ascensive force of air per square foot,

$$(34.68—18.86) \div 9.62 = 1.64 \text{ lbs.}$$

Total head in terms of cold air,

$$1.64 \div (1.293 \div 16) = 20.3 \text{ ft.} \qquad (5)$$

In terms of water gauge pressure,

$$20.3 \times 12 \div 772 = 0.32 \text{ in.} \qquad (5)$$

(6) Velocity of issuing gases, per second, at 250° C.,

$$92{,}880 \times \frac{250+273}{273} \div 3{,}600 \div 9.62 = 5.14 \text{ ft}$$

Head as velocity in terms of cold air at 0° C.,

$$(5.14)^2 \div 64.3 \times \frac{273}{273+250} \times 1.03 = 0.22 \text{ ft.}$$

In terms of water gauge pressure = 0.003 in.

(7) Average velocity of gases in chimney at 300° C.,

$$92{,}880 \div 3{,}600 \times \frac{300+273}{273} \div 9.62 = 5.63 \text{ ft.}$$

Head lost in friction in terms of cold air,

$$(5.63)^2 \div 64.3 \times \frac{273}{300+273} \times 1.03 \times \frac{49.5}{3.5} \times 0.08 = 0.27 \text{ ft.} \quad (7)$$

In terms of water gauge pressure = 0.004 in. (7)

(8)	*Cold Air.*	*Water Gauge.*	
Total head	20.30 feet	0.320 inch	
Absorbed in velocity of gases	0.22 "	0.003 "	
Absorbed in friction in chimney	0.27 "	0.004 "	
Available to draw gases in	19.81 "	0.313 "	(8)
(9)			
Available head needed for puddling (4)	43.50 "	0.664 "	
Available head needed for boiler	6.43 "	0.100 "	
Total head needed for both	49.93 "	0.764 "	
Available head from chimney (8)	19.81 "	0.313 "	
Deficit, to be supplied by blast	30.12 "	0.451 "	

(10) The 0.451 inches of water gauge equals

$$(0.451 \div 12) \times 62.5 = 2.35 \text{ lbs. per sq. ft.}$$

The volume of air to be supplied is, at 30° C.,

$$88{,}560 \text{ (Prob. 22)} \div 60 \times \frac{273+30}{273} = 1{,}638 \text{ cu. ft. per min.}$$

Net work done by the fan,

$$1{,}638 \times 2.35 = 3{,}850 \text{ ft. lbs. per min}$$

Gross power needed by the fan,

$$3{,}850 \div 0.25 \text{ (efficiency)} = 15{,}400 \text{ ft. lb. per min.}$$

Horse-power needed to drive the fan,

$$15{,}400 \div 33{,}000 = 0.47 \text{ H. P.} \quad (10)$$

(11) The boiler receives the gases at 1200° C. and discharges them at 350°, and 92.880 cubic feet of gases (measured at standard conditions) pass through per hour. The composition of these gases is not given, but from the specific gravity we might conclude that they contain on an average 10 per cent. of carbon dioxide, since if they contained the maximum amount

of that gas (about 20 per cent.) their specific gravity would be 1.06 (air = 1). Assuming them, therefore, to contain

CO^2.....10 per cent.
H^2O.....10 "
CO, N^2, O^2.....80 "

their heat capacity per degree per cubic foot would be, between 350° and 1200°.

CO^2 $0.1\times[0.37 + 0.00022\ (350+1200)] = 0.0711$ oz. cal.
H^2O $0.1\times[0.34 + 0.00015\ (350+1200)] = 0.0573$ "
CO, N^2, O^2 $0.8\times[0.303+0.000027(350+1200)] = 0.2759$ "

Sum = 0.4043 "

Heat given up per cubic foot,

$0.4043\times(1200—350) = 343.7$ oz. cal.

Heat given up by gases per hour to boiler,

$92{,}880\times343.7 = 31{,}922{,}850$ oz. cal.
$= 1{,}995{,}000$ lb. cal.

Heat in the steam produced per hour,

$1{,}995{,}000\times0.45$ (efficiency) = 897,750 lb. cal.

Heat equivalent of mechanical energy of steam engine per hour,

$897{,}750\times0.20$ (efficiency) = 179,950 lb. cal.
Heat equivalent of 1 hp hour = 635 kg. cal.
= 1,400 lb. cal.

Horse-power generated by the engine,

$179{,}950 \div 1{,}400 = 128$ H. P. **(11)**

(12) Net available power after supplying fan,

$128—0.5 = 127.5$ H. P. **(12)**

CHAPTER VIII.

CONDUCTION AND RADIATION OF HEAT.

These two factors are of the greatest practical importance to the metallurgist, yet they are also the subjects of all others upon which the practical metallurgist is usually the most poorly informed. It often happens that a furnace is built of twice the capacity of its predecessor or of its neighbors, and the manager unexpectedly and most agreeably discovers that it keeps up a more uniform heat and requires considerably less than twice the amount of fuel to keep it running. Two reasons were operative; first, the walls were made thicker to support the heavier structure, but that made them also poorer conductors of heat; second, the capacity increased as the cube of a linear dimension, while the radiating surface increased as its square, so that radiation was, therefore, less than twice the primary amount from the furnace of double capacity. Many practical metallurgists have learned the practical results, but are entirely ignorant of the principles upon which the results are obtained. While it is well to be successful, it is better to be intelligently so.

Principles of Heat Conduction.

It is well known that the ability of metals to conduct heat is very nearly the same as their ability to conduct electricity. The order of metals in these two series is almost identical. Further, the specific conductance for heat is closely analogous to specific conductance for electricity. Just as we say that the electrical resistance of a conductor is proportional to its length and inversely as its cross-section, so we can make the same statement concerning heat resistance. Just as we can add electrical *resistances* when the bodies are in series, and must add electrical *conductances* when they are in parallel, so we

can add heat resistances when the bodies are in line, and must add heat conductances when they are hooked up together in parallel.

The unit of electrical resistance is an ohm, and a substance has unit resistivity when a cube of it, 1 centimeter on a side, has that resistance. In such a case a drop of potential of 1 volt from one side to the opposite one sends through the cube 1 coulomb of electricity per second. Since conductivity is merely the reciprocal quality, actually and mathematically, to resistivity, the unit of conductivity is defined in exactly the same way, and the conductivity of any substance may be expressed as so many reciprocal ohms.

If we read in the preceding paragraph, thermal resistance for electrical resistance, degrees temperature for volts, and gram calories for coulombs, we have defined the corresponding unit of thermal resistivity. A substance has unit capacity for conducting heat when a cube 1 centimeter on a side transmits 1 gram calorie of heat per second, with a drop of temperature from one surface to the other of 1° C. Many investigators have adopted slightly different units, such as 1-kilogram Calorie per cubic meter per hour per degree difference; but such are only simple multiples or fractions of the centimeter-gram-second unit above defined.

Illustration: If the thermal conductivity of copper is 0.92 units, what would be the amount of heat passing per hour through a sheet 1 millimeter thick and 1 meter square, with a constant difference of 1° C. between the two sides?

Solution: The 0.92 units means that a column of copper 1 centimeter long and 1 square centimeter in cross-section, having a difference of temperature at its two surfaces of 1° C., would allow 0.92 gram-calories of heat to flow through it per second. For a sheet one-tenth as thick, 10,000 times the area and during 1 hour, the heat passing per 1° C. difference will be

$$0.92 \times \frac{10}{1} \times \frac{10{,}000}{1} \times 3600 = 331{,}200{,}000 \text{ cal.}$$

$$= 331{,}200 \text{ Cal.}$$

Such calculations as the above are, of course, very useful for comparing different thicknesses of plates of different material, as to their relative heat-carrying capacity. With some slight

modifications they are applicable to the actual conveyance of heat through such walls, from a fluid on one side to a fluid on the other. This introduces an idea analogous to transfer or contact resistance in electrolytic conduction. Thus, if we call R the thermal specific resistance (resistivity) in C. G. S. units, of the material of a partition having a thickness of d centimeters, and an area of S square centimeters, then the thermal resistance of the body of the partition will be

$$\frac{R \times d}{S}$$

and its thermal conductance

$$\frac{S}{R \times d} = k$$

Besides this resistance in the body of the material there is transfer resistance at its two sides, or at its inner and outer surfaces, which depends on the materials which communicate heat and receive heat, and their velocity. These resistances may be expressed as so many units per square centimeter, the unit being of exactly the same nature as R, except that it connotes no thickness but merely a surface effect. Calling R^1 the specific resistance of transfer from the inner fluid to the inner surface of the material, and R^2 the outside specific transfer resistance to the fluid outside, we can consider all three resistances as being in series, and the total thermal resistance to transfer from the inside fluid to the outside fluid to be

$$\frac{R \times d}{S} + \frac{R^1}{S} + \frac{R^2}{S}$$

or the thermal conductance of the system

$$\frac{S}{(R \times d) + R^1 + R^2} = k$$

The following table gives the thermal resistivity of various materials, in C. G. S. gram-Calorie units, also the thermal conductivity in units which are reciprocals of the resistance units:

Material.	*Conductivity (in reciprocal resistance units.)*	*Resistivity (in C.G S. gram-cal. units.)*
Silver (at 0°)	1.10	0.91
Copper (0°—30°)	0.92	1.09
Copper, commercial	0.82	1.22
Copper, phosphorized	0.72	1.39
Magnesium	0.38	2.63
Aluminium (0°)	0.34	2.94
Aluminium (100°)	0.36	2.75
Zinc (15°)	0.30	3.33
Brass, yellow (0°)	0.20	5.00
Brass, yellow (100°)	0.25	4.00
Brass, red (0°)	0.25	4.00
Brass, red (100°)	0.28	3.57
Cadmium (0°)	0.20	5.00
Tin (15°)	0.15	6.67
Iron, wrought (0°)	0.21	4.76
Iron, wrought (100°)	0.16	6.25
Iron, wrought (200°)	0.14	7.14
Iron, steel, soft	0.11	9.01
Iron, steel, hard	0.06	16.67
German silver (0°)	0.07	14.28
German silver (100°)	0.09	11.11
Lead (0°)	0 084	11.90
Lead (100°)	0.076	13.16
Antimony (0°)	0.044	22.73
Mercury (0°)	0.015	66.67
Mercury (50°)	0.019	52.63
Mercury (100°)	0.024	41.67
Bismuth (0°)	0.018	55.55
Wood's alloy (7°)	0.032	31.25
Alloy, 1 Sn. 99 Bi	0.008	125.00

The last alloy, bismuth, with only 1 per cent. of tin, is remarkable for its extremely low heat conductivity, less than one hundredth as good as copper. It has also the lowest electrical conductivity of any alloy, about one two hundredth that of copper. These peculiar properties ought to make it of use for some particular purposes.

The above data enables one to calculate the rate at which heat

will pass through a metallic partition or wall when the temperature of its two surfaces is known. This is a very useful calculation, for in many cases the temperature inside a partition or pipe is known, or can be easily determined, and when the temperature of the outside surface is determined, the calculation can be made. The temperature of the outside of a partition or pipe can be found by several methods: one is to lay a very flat bulb thermometer (made especially for this purpose) against it; another is to put the junction of a thermocouple against it, covering the couple with a little putty or clay; another is to take small pieces of metals, or alloys of known melting points, and see which melts against the hot metal. The only uncertainty then in the calculation is the question as to what difference in the conductivity may be caused by the higher temperature. The conductivities in most cases decrease as temperature rises, but in others increase. There is here a large field for metallurgical experiment, in determining the heat conductivities of metals, alloys and fire-resisting materials at high temperature.

Illustration: An iron pipe, 6 centimeters in diameter outside and 5 centimeters inside, is filled with water at 10° C., and surrounded by hot gases at 198° C. From the rise in temperature of the water it is known that for each square centimeter of heating surface 0.084-gram calories of heat pass per second. Assuming the thermal conductivity of the iron (k) = 0.14, what is the difference of temperature of the two surfaces, inside and outside, of the pipe?

Solution: The thickness of the walls is $(6—5) \div 2 = 0.5$ centimeter. If the walls were 1 centimeter thick, 1° difference would transmit 0.14 calorie; but being only half that thick, 1° difference would transmit 0.28-gram calorie. The actual difference of temperature of the two surfaces must then be

$$\frac{0.084}{0.28} = 0.3° \text{ C.}$$

Of course, such calculations can be turned around, and if the temperature of the inside and outside surfaces is known, the heat being transmitted can be calculated; or if the temperature of these two surfaces is known and the heat being transmitted is measured, the thermal conductivity of the partition can be

reckoned; or, again, if the temperature of the two surfaces is known, and also the thermal conductivity of the partition, and the temperature of either fluid on either side, the thermal resistance of the transfer from either of the fluids to the surface of the partition can be calculated.

Illustration; In the previous illustration the temperature of the hot gases was 198°, while that of the pipe in contact with them was practically 10°. What was the thermal resistivity of the transfer from gas to metal?

Solution: The thermal resistivity is the reciprocal of the thermal conductivity, and in the case of this transfer resistance is the reciprocal of the number of gram calories which will be transferred to 1 square centimeter of pipe surface from the hot gases per second per each degree centigrade of difference of temperature causing the flow. This is a surface or skin resistance, and, therefore, no linear dimension representing thickness enters into the calculation. There is 0.084 calorie per second being transferred to each square centimeter of pipe, with a difference of temperature acting as propelling force of 198—10 = 188°. The thermal conductivity of this transfer, k, is, therefore,

$$0.084 \div 188 = 0.00045$$

And the thermal resistivity, R, the reciprocal, viz.: 2222. Since the thermal resistivity of the iron wall is $1 \div 0.28 = 3.57$ units, it follows that the contact surface offers $2222 \div 3.57 = 622$ times as much resistance to the flow of heat as the metal itself. In this specific instance, we can conclude that the transfer of heat from the gases to the pipe is the principal item which conditions the flow of heat, the passage of the heat through the wall of the pipe itself taking place 622 times as readily.

The valuable practical conclusion is that the thermal resistance of the walls of the pipe is insignificant as compared with the whole thermal resistance, and the thickening or thinning of the walls of the pipe, or the substitution of copper for iron, because of its greater thermal conductivity, is practically unnecessary for thermal considerations, since such can be expected to make practically no change in the thermal resistance of the whole system.

If the pipe under discussion, however, acquires during use a

layer of scale deposited from the water, then the thermal resistance of the pipe or of the system is materially affected. A study of the thermal resistivity of various boiler scales would be a very useful and practical subject, but has not been done, as far as the writer is aware. Assuming a deposit, 0.5 centimeter thick, of material having the thermal conductivity of plaster of paris, for which k = 0.0013, the specific resistance of this material is $0.14 \div 0.0013 = 108$ times that of iron, and therefore 0.5 centimeter of this represents 54 centimeters thickness of iron. The thermal resistances in this case, neglecting that of transfer from the water to the pipe or scale, are as follows:

Resistance of transfer, gases to pipe = 2222.0 = 85 per cent.

Resistance of 0.5 c.m. iron $= \frac{0.5}{0.14} =$ 3.6 = 0 "

Resistance of 0.5 c.m. scale $= \frac{0.5}{0.0013} =$ 384.4 = 15 "

Total = 2610.0

It thus appears that a deposit of scale from the water to a thickness of 5 millimeters increases the total thermal resistance of the system some 18 per cent. of its original amount, and would cut down the efficiency of this part of the heating surface of a boiler by this amount. These considerations are not only of vital importance to the steam boiler engineer, but they are the essential principles which condition the efficiency of steam-heating apparatus, feed-water heaters, hot-air stoves and ovens, air-cooling of parts of furnaces and the efficiency of water jackets.

Principles of Heat Transfer.

We have already had to speak of the transfer of heat from fluids to solids, or *vice versa*, and in one specific case we deduced the value 2222 for the transfer resistivity from hot gases to the surface of iron pipe, meaning thereby that for each degree of temperature difference between the gases and outside of the pipe 0.00045 gram calorie passed per second through each square centimeter of contact surface. A consideration of the transfer of heat through such contact surfaces, from gases or liquids to solids and *vice versa*, has shown that the

transfer resistivity varies with the solid and with the fluid concerned, but much more with the latter than with the former, and is very largely dependent upon the circulation of the fluid, that is, upon the rate at which it is renewed, and therefore upon its velocity. The conductivity or resistivity of such a transfer must, therefore, contain a term which includes the velocity of the fluid. Various tests by physicists have shown the specific conductance (or conductivity of transfer) to vary approximately as the square root of the velocity of the fluid.

From metal to air or similar gases, the mean velocity of flow being expressed in centimeters per second, and the other units being square centimeters and gram calories, the transfer resistivity is approximately

$$R = \frac{36{,}000}{2+\sqrt{v}}$$

and the transfer conductivity of the contact

$$k = 0.000028\ (2+\sqrt{v})$$

From hot water to metal the relations are similar, but the conductivity is much better Experiments show values as follows:

$$k = 0.000028\ (300+180\sqrt{v})$$

$$R = \frac{36{,}000}{300+180\sqrt{v}}$$

Illustration: In the preceding case of the iron pipe, calculate the difference of temperature of the water in the pipe and the inner surface of the pipe, assuming the water to be passing through at a velocity of 4 centimeters per second.

Using the above given formula, the heat transfer per 1° difference would be

$$0.000028\ (300+180\sqrt{4}) = 0.0185 \text{ calories},$$

and the difference to transfer 0.084 calories per second will be

$$\frac{0.084}{0.0185} = 4°.6$$

The inner surface of the iron pipe will be, therefore, continuously 4°.6 higher than the water, and, therefore, at 14°.6;

the outer surface will be continuously 0°.3 higher, or practically at 15°.

Illustration: A steam radiator, surface at about 100° C., caused a current of hot air to rise having a velocity of about 10 centimeters per second, which was insufficient to keep the room warm. An electric fan was set to blow air against the radiator, which it did with a velocity of about 300 c.m. per second, and keeping the room comfortably warm. What were the relative quantities of heat taken from the radiator in the two cases?

The relative thermal conductivities of transfer were

$$2+\sqrt{10} : 2+\sqrt{300}$$

or

$$5 : 16$$

Showing over three times as much heat taken away per unit of time in the second instance.

This illustration proves the great efficiency which the metallurgist may attain in air cooling of exposed surfaces, by blowing the air against them instead of merely allowing it to be drawn away by its ascensive force.

Problem 24.

Dry air of the volume of 33,000 cubic meters per hour passes through an iron pipe exposed to the air, 30 meters long, 1.5 meters inside diameter, thickness of walls 1 centimeter, and lined inside with 5 centimeters of fire-brick. Assume the hot air entering at 1,000°, the outside air to be at 3°, the coefficient of internal transfer 0.000028 $(2+\sqrt{v})$, the conductivity of the fire-bricks 0.0014, of the iron 0.14, of external transfer 0.000028 $(2+\sqrt{v})$, the velocity of the wind against the outside 10 kilometers per hour.

Required: The temperature of the hot air leaving the tube.

Solution: The mean temperature in the tube is the factor which conditions the mean velocity in the tube, and the rate of flow of heat towards the outside. If, therefore, we let t represent that mean temperature, the solution can be stated in the simplest terms. We then have:

Volume of air per hour, at 0°, = 33,000 cubic m.
Volume of air per second, at 0°, = 9.167 "

Volume of air per second, at t, $= 9.167 \frac{t+273}{273}$

Cross-section of inside of tube
$(1.5—0.1)^2 \times 0.7854 = 1.54$ sq. m.

Velocity of air at t, in pipe

$$9.167 \frac{t+273}{273} \div 1.54 = 5.95 \left(\frac{t+273}{273}\right) \text{ m. p. s.}$$

$$= 5.95\ (1+\alpha t) \text{ m. p. s.}$$

$$= 595\ (1+\alpha t) \text{ c.m. p. s.}$$

Coefficient of internal transfer $=$

$$0.000028\ (2+\sqrt{595\ (1+\alpha t)})$$

Coefficient of conductance of 5 c.m. of fire-brick lining $=$

$$0.0014 \div 5 = 0.00028$$

Coefficient of conductance of 1 c.m. of iron $=$

$$0.14 \div 1. = 0.14$$

Coefficient of external conductance (v = 278 c.m. per sec.) $=$

$$0.000028\ (2+\sqrt{278}) = 0.000524$$

Total fall of temperature of air $= 2\ (1000—t)$

End temperature of the air $= 1000—2\ (1000—t)$

$$= 2\,t—1000$$

Mean specific heat of air per cubic meter between 1000 and end temperature $=$

$$0.303+0.000027\ (2t)$$

Heat given out by the air per hour $=$

$$33{,}000 \times 2(1000—t) \times (0.303+0.000027\ (2t)) =$$

$$19{,}998{,}000—16{,}434\,t—3.564\,t^2$$

This heat is the quantity transferred through the pipe in kilogram Calories. The outside surface of the pipe may be taken as the conducting surface, because the larger part of the resistance to the flow of heat takes place there. If we desired to be more exact, the mean area of iron, fire-bricks and the inner surface could be each used separately. The outside diameter being 150 centimeters, and the length 30 meters, the outer surface is $1.52 \times 3.1416 \times 30 = 142.3$ square meters $=$ 1,423,000 square centimeters, the total driving force is the inside temperature minus that outside, or t—3, and the total

thermal resistance is the sum of the four thermal resistances in series, that is, the sum of thermal resistance gas to fire-bricks =

$$\frac{1}{0.000028\ (2+\sqrt{595\ (1+\alpha\ t)}}$$

thermal resistance of fire-brick lining =

$$\frac{1}{0.00028}$$

thermal resistance of iron shell =

$$\frac{1}{0.14}$$

thermal resistance of iron to air =

$$\frac{1}{0.000524}$$

The reciprocal of the sum of these four resistances is the thermal conductance of the system per square centimeter, which, multiplied by the conducting surface, 1,423,000 square c.m., and by the total difference of temperature, t—3, gives the heat transferred per second in gram calories.

We, therefore, have the final equality expressed as the heat given up by the air, per second, equals the heat transmitted to the outside air per second; *i.e.*,

$$\frac{1000}{3600}\ (19{,}998{,}000-16.434\ t-3.564\ t^2) =$$

$$\frac{1}{\frac{1}{0.000028\ (2+\sqrt{595\ (1+\alpha t)}} + \frac{1}{0.00028} + \frac{1}{0.14} + \frac{1}{0.000524}} \times 1{,}423{,}000 \times (t-3)$$

Whence $t = 965°.5$

And the temperature of the air at the end of the tube is

$$2t-1000 = 931° \qquad (1)$$

It would be interesting to compare the temperatures of the inside and outer surfaces of the tube. The air inside is at a mean temperature of 965°, the heat transmitted per second is 0.1574-gram calories per square centimeter of outer surface,

whose thermal conductivity is 0.000515, and therefore, the outside surface must be

$$\frac{0.1574}{0.000515} = 306°$$

hotter than the surrounding air; that is, must be at 309° C.

The extra loss of heat by radiation from this outside surface would be small at that low temperature, but has not been allowed for in the working of the problem.

For such metallurgical problems we need the data as to the thermal conductivity or resistivity of ordinary furnace materials. These have been determined in but few instances, and in most cases not at the high temperatures at which they are practically used. A whole series of physico-metallurgical experiments is needed just upon this point. The following are probably nearly all that have been determined and the values published. The unit k is the C. G. S.-gram calories unit, the same as used for the metals.

	k.
Ice (datum useful in refrigerating plants, where pipes become coated with ice, as in Gayley's method of drying blast)	0.00500
Snow	0.00050
Glass (10°—15°)	0.00150
Water	0.00120
Quartz sand (18°—98°)	0.00060
Carborundum sand (18°—98°)	0.00050
Silicate enamel (20°—98°)	0.00040
(Explains the small conductance of enameled iron ware.)	
Fire-brick, dust (20°—98°)	0.00028
Retort graphite dust (20°—100°)	0.00040
(Datum useful where articles are packed in this poorly conducting material.)	
Lime (20°—98°)	0.00029
(Datum would be highly useful for oxyhydrogen platinum furnaces, if it were only known at high temperatures.)	
Magnesia brick, dust (20°—100°)	0.00050
Magnesia calcined, Grecian, granular (20°—100°)	0.00045

Masonry	0.0036 to 0.0058
Water, uncirculated	0.0012 to 0.0016

Magnesia calcined, Styrian, granular (20°—100°)	0.00034
Magnesia calcined, light, porous (20°—100°)	0.00016
Infusorial earth (Kieselguhr) (17°—98°)	0.00013
Infusorial earth (0°—650°)	0.00038
Clinker, in small grains (0°—700°)	0.00110
Coarse ordinary brick dust (0°—100°)	0.00039
Chalk (0°—100°)	0.00028
Wood ashes (0°—100°)	0.00017
Powdered charcoal (0°—100°)	0.00022
Powdered coke (0°—100°)	0.00044
Gas retort carbon, solid (0°—100°)	0.01477
Cement (0°—700°)	0.00017
Alumina bricks (0°—700°)	0.00204
Magnesia bricks (0°—1300°)	0.00620
Fire-bricks (0°—1300°)	0.00310
Fire-bricks (0°—500°)	0.00140
Marble, white (0°)	0.0017
Pumice	0.0006
Plaster of paris	0.0013
Felt	0.000087
Paper	0.00040
Cotton	0.000040
Wool	0.000035
Slate	0.00081
Lava	0.00008
Pumice	0.00060
Cork	0.00072
Pine wood	0.00047
Oak wood	0.00060
Rubber	0.00047

A study of the above table will in many cases show the metallurgist how conduction of heat can be checked, and to what degree. The substance chosen must be able to stand the temperature without being destroyed; but it is in many cases possible to use one kind of material inside, where the heat is greatest, and a material of much poorer conductivity outside, where the heat will not destroy it. Such compound linings or coverings may be very advantageous. Infusorial earth is one of the very best insulators for moderate temperature; above

a bright red it loses efficiency greatly, and is then hardly better than powdered fire-brick.

Mr. Irving Langmuir has recently conducted important experiments on convection and radiation of heat, recorded in a paper before the American Electrochemical Society (Transactions (1913) **23,** 299–332). His experimental results for convection alone, from horizontal and vertical surfaces, to still air at 27° C., are as follows, first in calories per second and next in watts:

GRAM-CALORIES PER SEC. PER SQ. CM.—TO STILL AIR AT 27° C.

		100°	200°	300°	400°	500°
Downward	from — Surface	0.002	0.014	0.024	0.035	0.047
	from | Surface	0.005	0.029	0.050	0.074	0.099
Upward	from — Surface	0.011	0.032	0.055	0.081	0.108

WATTS PER SQ. CM.—TO STILL AIR AT 27° C.

		100°	200°	300°	400°	500°
Downward	from — Surface	0.010	0.060	0.100	0.146	0.196
	from | Surface	0.020	0.120	0.210	0.308	0.416
Upward	from — Surface	0.046	0.132	0.233	0.341	0.452

These figures are for convection alone, and do not include radiation. They are different from the formula given on page 207, but are probably more reliable. If data are required for over 500°, the above values may be plotted and the curves extrapolated.

If the air is in motion, Mr. Langmuir found that the heat loss by convection could be expressed as $\sqrt{\frac{35+V}{35}}$ times the loss to still air, where V is the velocity of air current in centimeters per second. Therefore, the velocity being known, evaluate the above expression and multiply the tabulated values by this factor.

RADIATION.

A body placed in a vacuum, with no ponderable substance in contact with it, radiates heat to its surroundings. All experiments so far made confirm the accuracy of Stefan's law, that every hot body radiates energy in proportion to the fourth power of its absolute temperature, and that the transfer of heat by radiation is therefore proportional to the difference

between the fourth powers of the absolute temperatures of the hot body and its surroundings, respectively.

Mr. Langmuir uses Stefan's law of radiation expressed in the following form

$$Q_R = E\ 5.9 \times 10^{-12}(T_2^4 - T_1^4) \text{ watts per sq. cm.}$$
$$= E\ 1.41 \times 10^{-12}(T_2^4 - T_1^4) \text{ cal. per sec. per sq. cm.}$$

These formulæ express the fact that the radiation from a body at absolute temperature T_2 to one at T_1, is proportional to the difference between the fourth powers of the temperatures in question, and that for each unit of such difference the radiation loss from the hotter body is 1.41×10^{-12} calories per square centimeter per second, if the body has unity radiating power (black body), or $E \times 1.41 \times 10^{-12}$ calories if its coefficient of radiating power (emissivity) is E. If the heat flow is expressed as energy flow, 1.41 calories per second $= 5.9$ watts.

For convenience sake, to avoid large numbers, the absolute temperatures may be expressed on a scale of 1000°, in which case 10^{-12} disappears, and the formula becomes:

$$Q_R = E \times 5.9 \left[\left(\frac{T_2}{1000}\right)^4 - \left(\frac{T_1}{1000}\right)^4\right] \text{ watts}$$
$$= E \times 1.41 \left[\left(\frac{T_2}{1000}\right)^4 - \left(\frac{T_1}{1000}\right)^4\right] \text{ cal. per sec.}$$

In the above form, this formula is very convenient for calculating radiation losses from any body at absolute temperature T_2 to its surroundings at T_1, provided the emissivity of the hot body, E, is known. Dull lampblack has an emissivity nearly 1.00, but all other materials have emissivities less than unity, the polished metals having values as low as 0.02. Unfortunately, total energy emissivity is not quite independent of temperature, and most of the determinations have been made for low temperatures only.

In the following table, some emissivities have been calculated from the older experiments on radiation, and some are Mr. Langmuir's own values.

Radiating Capacity (Emissivity) = E

Theoretical black body.	(At all temperatures) = 1.00			
Lampblack	(50°) 0.95 – 0.98			
Smoothblack paint	(50°) 0.68			
Black paper	(50°) 0.64			
Cast iron, rusted	(50°) 0.56	(300)° 0.67	(500)° 0.53	
Cast iron, new	(50°) 0.52			
Cast iron, polished	(50°) 0.17			
Cast iron, liquid	(1200°) 0.28	(1750°) 0.28	(Thwing)	
Soft steel, liquid	(1600°) 0.28			
Iron oxide scale	(500°) 0.85	(1000°) 0.88	(1200°) 0.89	
Iron rust	(440°) 0.91	(468°) 0.85		
Russian sheet iron	(50°) 0.56			
Ordinary sheet iron	(50°) 0.47			
Leaded sheet iron	(50°) 0.11			
Tinned sheet iron	(50°) 0.04			
Hematite	(500°) 0.98			
Chromite	(50°) 0.99	(1000°) 0.99		
Cuprous oxide	(50°) 0.60	(720°) 0.60	(945°) 0.60	(1170°) 0.61 (Burgess)
Graphite, polished	(50°) 0.65	.....	.....	(500°) 0.95
Graphite, mat	(50°) 0.90	(300°) 0.82	(400°) 0.92	
Copper, oxidized	(50°) 0.77	(300°) 0.70	(500°) 0.73	(1000°) 0.70
Copper, calorized	(50°) 0.39	(300°) 0.26	(500°) 0.23	(1000°) 0.20
Copper, polished	(50°) 0.03	(1000°) 0.09		
Copper, liquid	(1075°) 0.16	(1175°) 0.15	(1275°) 0.13	(1290°) 0.15 Thwing
Aluminium polished	(240°) 0.156	(360°) 0.19		
Aluminium paint	(50°) 0.67	(127°) 0.45		
Brass, polished	(50°) 0.04			
Silver, polished	(50°) 0.02	(300°) 0.03	(500°) 0.04	
Gold, polished	(50°) 0.03	(500°) 0.07		
Gold, enamel	(50°) 0.33	(126°) 0.37		
Platinum, polished	(50°) 0.035	(300°) 0.061	(500°) 0.08	(1000°) 0.124
	(1160°) 0.14	(1430°) 0.16	(1695°) 0.175	(Burgess)
Silvered paper	(50°) 0.07			
Monel metal, bright	(50°) 0.50	(300°) 0.30		
Monel metal, oxidized	(50°) 0.50	(300°) 0.41	(500°) 0.38	
Chromium	(50°) 0.11	(500°) 0.19	(1000°) 0.37	
Zinc, bright	(50°) 0.04			
Nickel, bright	(50°) 0.05	(500°) 0.06	(1000°) 0.17	
Nickel oxide	(50°) 0.35	(300°) 0.40	(500°) 0.48	(710°) 0.62
	(800°) 0.68	(1000°) 0.75	(1075)° 0.80	(1300°) 0.88
Tin, bright	(50°) 0.04			
Magnesium	(50°) 0.07	(300°) 0.14	(500°) 0.23	
Silicon	(50°) 0.72	(1000°) 0.72		
Tungsten	(3250°) 0.39	(Langmuir).		
Alumina	(500°) 0.10			
Zirconia	(50°) 0.06	(500°) 0.09		
Magnesia	(50°) 0.06	(500°) 0.09		
Lime	(50°) 0.10	(500°) 0.40		
Glass	(50°) 0.49			
Porcelain	(50°) 0.25	(500°) 0.50		
White fire clay	(300°) 0.73	(400°) 0.79		
Building stone	(50°) 0.60			
Plaster	(50°) 0.60			
Wood	(50°) 0.60			

APPENDIX TO PART I.

Problem 25.

(1) Write the equations showing the relative weights and relative volumes (of gases) concerned in the combustion of

Methane (marsh gas).....$C\ H^4$
Acetylene.....$C^2\ H^2$
Ethylene (olefiant gas).....$C^2\ H^4$
Methylene.....$C^2\ H^6$
Allylene.....$C^3\ H^4$
Propylene.....$C^3\ H^6$
Propylene hydride.....$C^3\ H^8$
Benzine.....$C^6\ H^6$
Turpentine (liquid).....$C^{10}H^{16}$
Napthaline (liquid) .....$C^{10}H^8$

(2) The molecular heats of combustion of the above gases to CO^2 and liquid H^2O are given by Berthelot as:

for $C\ H^4$.....213,500 Calories
" $C^2\ H^2$.....315,700 "
" $C^2\ H^4$ .....341,100 "
" C^2H^6 .....372,300 "
" $C^3\ H^4$.....473,600 "
" $C^3\ H^6$.....499,300 "
" $C^3\ H^8$..... .....528,400 "
" $C^6\ H^6$.....784,100 "
" $C^{10}H^{16}$ (liquid).....1,490,800 "
" $C^{10}H^8$ (liquid).....1,241,800 "

(a) Calculate the molecular heats of combustion to CO^2 and H^2O vapor.

(b) Calculate the molecular heats of formation of the hydrocarbons themselves, using (C, O^2) 97,200 and (H^2O) 69,000 liquid or 58,060 gas.

(c) Calculate the heat of combustion, to CO^2 and H^2O vapor, of one cubic meter of each gas, and of one cubic foot in B. T. units.

Answers (1):

I		II		I		II	
CH^4	+	$2O^2$	=	CO^2	+	$2H^2O$	
16		64		44		36	
II		V		IV		II	
$2C^2H^2$	+	$5O^2$	=	$4CO^2$	+	$2H^2O$	
52		160		176		36	
I		III		II		II	
C^2H^4	+	$3O^2$	=	$2CO^2$	+	$2H^2O$	
28		96		88		36	
II		VII		IV		VI	
$2C^2H^6$	+	$7O^2$	=	$4CO^2$	+	$6H^2O$	
60		224		176		108	
I		IV		III		II	
C^3H^4	+	$4O^2$	=	$3CO^2$	+	$2H^2O$	
40		128		132		36	
II		IX		VI		VI	
$2C^3H^6$	+	$9O^2$	=	$6CO^2$	+	$6H^2O$	
84		288		264		108	
I		V		III		IV	
C^3H^8	+	$5O^2$	=	$3CO^2$	+	$4H^2O$	
44		160		132		72	
I		XIV		X		VIII	
$C^{10}H^{16}$	+	$14O^2$	=	$10CO^2$	+	$8H^2O$	
136		448		440		144	
I		XII		X		IV	
$C^{10}H^8$	+	$12O^2$	=	$10CO^2$	+	$4H^2O$	
128		384		440		72	

(2)

	Molecular Heat of Formation (C Amorphous.)	*Molecular Heat of Combustion (to H^2O Vapor.)*	*Heat of Combustion of 1 m^3 (Cal.)*	*1 $ft.^3$ B.T.U.*
$C\ H^4$	+21,700	+ 191,620	+ 8,623	+ 970
$C^2\ H^2$	—52,300	+ 304,760	+13,714	+1,543
$C^2\ H^4$	— 8,700	+ 319,220	+14,365	+1,616
$C^2\ H^6$	+29,100	+ 339,480	+15,277	+1,719
$C^3\ H^4$	—44,000	+ 451,720	+20,327	+2,287
$C^3\ H^6$	— 700	+ 466,480	+20,992	+2,362
$C^3\ H^8$	+39,200	+ 486,640	+21,899	+2,464
$C^6\ H^6$	+ 6,100	+ 751,280	+33,808	+3,803
$C^{10}H^{16}$ (liquid)	+33,200	+1,403,280	....	....
$C^{10}H^{16}$ (gas)	+23,800	+1,412,680	+63,570	+7,152
$C^{10}H^8$ (liquid)	+ 6,200	+1,198,040	....	....

Problem 26.

The following typical analyses are from Poole's book on "The Calorific Power of Fuels":

	Bituminous Coal. "Carnegie, Pa."	*Fuel Oil.* "Lima, O."	*Natural Gas.* "Findlay, O."	
Carbon	77.20	80.2	H^2	1.64
Hydrogen	5.10	17.1	CH^4	93.35
Oxygen	7.22	1.3	C^2H^4	0.35
Nitrogen	1.68	1.4	CO^2	0.25
Sulphur	1.42		CO	0.41
Moisture	1.45		O^2	0.39
Ash	5.93		N^2	3.41
			H^2S	0.20

Required: (1) The practical, metallurgical calorific powers of

(a) The coal, per kilogram or pound 7,447

(b) The oil, per kilogram or pound 11,393

(c) The gas, per cubic meter 8,143 kg. Cal.

(d) The gas, per 1000 cubic feet 509,000 lb. Cal.

(2) Compare the calorific values of 1 ton (2240 lbs.) of coal, 1 ton (2000 lbs.) of oil, and 1000 cubic feet of natural gas.

32.8:44.8:1.

Problem 27.

The composition of some commercial gases used as fuels is given by Wyer (Treatise on Producer-Gas and Gas Producers, p. 50), as in following table:

	H^2	CH^4	C^2H^4	N^2	CO	O^2	CO^2
Natural gas (Pittsburg)	3.0	92.0	3.0	2.0			
Oil gas	32.0	48.0	16.5	3.0		0.5	
Coal gas, from retorts	46.0	40.0	5.0	2.0	6.0	0.5	0.5
Coke-oven gas	50.0	36.0	4.0	2.0	6.0	0.5	1.5
Carburetted water-gas	40.0	25.0	8.5	4.0	19.0	0.5	3.0
Water gas	48.0	2.0		5.5	38.0	0.5	6.0
Producer gas (hard coal, using steam)	20.0			49.5	25.0	0.5	5.0
Producer gas (soft coal)	10.0	3.0	0.5	58.0	23.0	0.5	5.0

Requirements: For each of the above gases calculate

(1) The volume of air theoretically necessary to burn it.

(2) The volume of the products of combustion.

(3) The calorific power

(a) per cubic meter, in kilogram Calories.

(b) per cubic foot, in pound Calories.

(c) per cubic foot, in British Thermal Units.

(4) The theoretical temperature, if burned cold with cold air (calorific intensity).

Results:

	Volume of air to burn 1 volume.	*Volume of products per 1 volume*	*Calorific Power. Kg. Cal. per m³.*	*Lb. Cal. per ft³.*	*B.T.U. per ft³.*	*Calorific Intensity.*
Natural gas (Pittsburg)	9.35	10.33	8423	526	948	1852°
Oil gas	7.74	8.58	7350	460	828	1915°
Coal gas, from retorts	5.79	6.50	5550	347	625	1896°
Coke-oven gas	5.36	6.08	5159	322	579	1892°
Carburetted water-gas	5.06	5.77	5008	313	563	1914°
Water gas	2.24	2.81	2590	162	292	1928°
Producer gas (with steam)	1.08	1.86	1290	81	146	1676°
Producer gas (ordinary)	1.13	1.98	1300	82	148	1555°

Problem 28.

An anthracite coal containing on analysis

Carbon	89 per cent.
Hydrogen	3 "
Oxygen	1 "
Ash	7 "

is burned under a boiler, and the ashes produced weigh, dry, 10 per cent. of the weight of the coal used. The chimney gases, dried and then analyzed, contain CO^2 15.3 per cent., O^2 3.5 per cent., N^2 81.2 per cent., and 25.9 grams of water is obtained for each cubic meter of dry gas collected.

Required: (1) The volume of chimney gas (measured dry) produced per kilo. of coal burned 10.41 m³.

(2) The volume of air used, measured dry at normal conditions, per kilo. of coal burned 10.67 m³.

(3) The weight of dry air used 13.80 kg.

(4) The volume of dry air theoretically necessary for the complete combustion of one kilo. of coal 8.72 m³.

(5) The excess of air used, in percentage of that theoretically necessary for the perfect combustion of the coal 22.36%.

(6) The volume of chimney gas, at standard conditions, per kilo. of coal burned 10.74 m^3.

Problem 29.

An anthracite coal contains

Carbon	89 per cent.
Hydrogen	3 "
Oxygen	1 "
Ash	7 "

It is burned on a grate, using 15 per cent. more air than is theoretically needed for its perfect combustion. The ashes weigh 10 kilos. per 100 kilos. of coal burned.

Required: (1) The volume of air (assumed dry and at standard conditions) used per kilo. of coal burned 9.71 m^3.

(2) The number of cubic feet of air per pound of coal 155.4.

(3) The percentage composition (by volume, of course) of the chimney gas, assuming it contains no soot or unburned gas. N^2 77.9, CO^2 16.1, O^2 2.6, H^2O 3.4.

(4) The percentage composition of the same, if first dried and then analyzed N^2 80.6, CO^2 16.7, O^2 2.7.

(5) The number of grams of moisture carried per cubic meter of dried gas measured 28.4.

(6) The number of grains per cubic foot 12.4.

(7) The volume of the chimney gases, at standard conditions, (water assumed uncondensed) per kilo. of coal burned 9.85 m^3.

(8) The number of cubic feet of products per pound of coal 157.6.

(9) The volume of the products in cubic meters at 350° C. and 700 m.m. pressure 24.4.

(10) The volume of the products in cubic feet at 600° F. and 29 inches pressure 349.6.

Problem 30.

A bituminous coal contains

Carbon	75 per cent.
Hydrogen	5 "
Oxygen	10 "
Ash	10 "

It is powdered and injected into a cement kiln with 25 per cent. more air than is theoretically necessary for its complete combustion. The kiln calcines 200 barrels of cement daily, using 125 pounds of coal per barrel of cement. Assume outside air at 0° C. Hot gases enter stack at 819° C. Omit from calculation the water vapor and carbonic acid gas expelled from the charge.

Required: (1) The volume of air per minute which the blower or fan must furnish. 2,672 ft³.

(2) The volume of the hot products of combustion per minute, as they pass into the stack. 11,044 ft³.

Problem 31.

A bituminous coal (as of Problem 30) contains

Carbon	75 per cent.
Hydrogen	5 "
Oxygen	10 "
Ash	10 "

It is burned under a boiler with 25 per cent. more air than is theoretically necessary for its complete combustion. Assume combustion perfect, and no unburnt carbon to remain in the ashes. The wet steam produced contains 3 per cent. of water of priming, and 8.82 pounds of water is evaporated per pound of coal burnt. Steam pressure 6 atmospheres effective pressure. Outside air 0° C., feed water 10° C., stack gases 310° C.

Required: (1) The calorific power of the coal, by calculation, water formed considered uncondensed, in pound calories per pound of coal, and British Thermal Units per pound. 7096; 12773.

(2) The percentage of the calorific power of the coal represented by the heat in the dry steam produced 78.0.

(3) ditto in the water of priming 0.6.

(4) ditto in the sensible heat of the chimney gases 14.5.

(5) ditto lost by radiation and conduction 6.9.

(6) What increase in the net efficiency (requirement 2) would be obtained by using a feed water heater, which abstracted 60 per cent. of the sensible heat in the chimney gases, all other conditions remaining constant? 8.6%.

Problem 32.

A bituminous coal contains (as in Problems 30 and 31):

Carbon	75 per cent.
Hydrogen	5 "
Oxygen	10 "
Ash	10 "

It is blown into a revolving cylindrical furnace with a high pressure blast which supplies only 14.9 per cent. of the air necessary for its complete combustion, producing near the burner a highly luminous flame surrounded by a cylindrical sheath of auxiliary air drawn in by the injector action of the fuel-air jet. Assuming that in the body of the jet the hydrogen only of the coal is consumed, the luminosity being due to unconsumed particles of carbon, and ash; that the mean specific heat of carbon is $0.5 - \frac{120}{t}$, of the ash 0.25

Required: (1) The theoretical temperature of the interior of the jet of burning fuel 1140°C.

(2) The temperature if the supply of air in the fuel jet is increased to that theoretically necessary for perfect combustion of the whole fuel . 1945°C.

Problem 33.

Calculate the maximum temperature obtainable in the region of the tuyers of a blast-furnace.

(1) Using cold, dry air.....1683° C.

(2) Using dry air, heated to 700° C. 2272° C.

(3) Using moist air, heated to 700° C., the amount of moisture present being such as air at 37° C. can carry when saturated with moisture. 1947° C.

(4) Using cold, moist air of above composition. 1367° C.

Problem 34.

Powdered coal having the following composition is burnt in a cement kiln:

Carbon	73.60 per cent.
Hydrogen	5.30 "
Nitrogen	1.70 "
Sulphur	0.75 "

Oxygen	10.00 per cent.
Ash	8.05 "
Moisture	0.60 "

The finely-ground coal is burnt by cold air, at 20° C., and 760 m.m. pressure. The gases resulting, together with carbon dioxide gas from the charge, pass into the stack at 820° C. The analysis of the flue gases, by volume, dried before analysis, is:

Carbon dioxide	25.9 per cent.
Oxygen	3.1 "
Carbon monoxide	0.2 "
Sulphur dioxide	not determined.
Nitrogen	difference.

Of the carbon dioxide in the gases assume 40 per cent. of it to come from the carbonates in the charge being treated, and not from the coal. Assume no water in the furnace charge. The air used is saturated with moisture, at 20° C., tension of the moisture 22 m.m. of mercury.

Required: (1) The theoretical calorific power of the coal 7090.

(2) The theoretical temperature of the hottest part of the flame 1593° C.

(3) The proportion of the calorific power of the fuel carried out by the hot gases 50.4%.

(4) The percentage excess of air admitted above that theoretically required 16.4%.

Problem 35.

Calculate the draft of a chimney, in inches of water gauge and feet of cold air, if measured at its base, its height being 120 feet, inside diameter, (round) 6 feet, temperature of gases inside at bottom 300° C., at top 200° C., specific gravity (air = 1) 1.03, and taking in 200 cubic feet (measured at 0° and 760 m.m.) of products of combustion per second. Section inside uniform top to bottom, sides fairly smooth, assume K = 0.04. Outside temperature 0° C. 0.91 in.; 59.25 ft.

Problem 36.

A copper cylinder weighing 22.092 grams was placed in a small iron box on the end of a rod, and held several minutes in the hot blast main of a blast-furnace. On removal, and drop-

ping instantly into a calorimeter, containing 301.3 grams of water, the temperature rose 4°.183 C. in three minutes. From previous experiments with this calorimeter, it was known that in three minutes it would abstract from the water 30 gram calories for each 1° observed rise of temperature above starting. The mean specific heat of copper between 0° and t° being $0.09393+0.00001778t$, what was the temperature of the hot-blast?

[N.B.—Calculate what would theoretically have been the temperature of the water of the calorimeter if no heat had been lost to the calorimeter, and work out using this as the final temperature of the water.] 618° C.

Problem 37.

A piece of tin-stone (Cassiterite, SnO^2) from Bolivia was tested to obtain its specific heat. It was heated to two temperatures determined by a Le Chatelier thermo-electric pyrometer, and dropped into a calorimeter. Corrections for calorimeter losses were made as explained in the *Journal of the Franklin Institute*, August, 1901. Data of the two tests were as follows:

	Experiment 1.	*Experiment* 2.
Weight of tin-stone used	12.765 gms.	12.765 gms.
Temperature of same	476° C.	1018° C.
Weight of water in calorimeter	299.4 gms.	300.7 gms.
Temperature of same, starting	16°.527	18°.705
Temperature of same, 3 minutes	18°.444	22°.986
Water value of calorimeter per 3′, for each 1° rise	30 cal.	30 cal.

Required: A formula of the form $S_m = \alpha+\beta t$, for the particular piece of Cassiterite used. $0.1050+0.0000061t$.

Problem 38.

The chimney gases from a boiler enter the stack at a temperature of 400° C. Their composition is:

Carbon dioxide	15.0 per cent.
Oxygen	5.9 "
Nitrogen	79.1 "

What percentage of the total calorific power of the coke burnt will be saved by using a feed-water heater which reduces the

temperature of these gases to 200° C. and sends 75 per cent. of the heat thus abstracted into the boiler with the feed-water? 7.92%.

Problem 39.

A blast-furnace gas contains, by volume:

Carbon monoxide	23 per cent.
Carbon dioxide	12 "
Hydrogen	2 "
Methane	2 "
Water vapor	3 "
Nitrogen	58 "

Its temperature is 20° C., and it is taken to a gas engine, mixed with the theoretical amount of dry air needed for perfect combustion, and compressed to 4 atmospheres tension (total pressure) before being ignited. Neglect the heating of the gas-air mixture by compression, *i.e.*, assume the temperature of the compressed mixture 20° C. before ignited. Assume that at the instant of ignition the volume occupied by the gases remains constant, so that the specific heat at constant volume applies. (Specific heat of 1 cubic meter at constant volume equals specific heat at constant pressure—0.09.)

Required: (1) The calorific power of the gas per cubic meter, at constant pressure, and at constant volume. 928.5; 925.5.

(2) The theoretical temperature at the moment after ignition has taken place. 1592° C.

(3) The maximum pressure exerted. 22⅔ atmospheres.

(4) The volume of gas needed per horse-power hour, at a mechanico-thermal efficiency of 30 per cent. 2.81 m^3, at 20° C.

Problem 40.

Bituminous coal containing carbon 78 per cent., hydrogen 5, oxygen 8, ash 8, water 1, is used in a gas producer. Assume the calorific power of the coal (water formed uncondensed) as 7480 Calories; ashes formed 12 per cent. Gas formed leaves producer at 600° C.; composition:

Carbon monoxide	35 per cent.
Carbon dioxide	5 "
Methane	5 "
Hydrogen	5 "
Nitrogen	50 "

Required: (1) The volume of gas obtained per kilo. of coal burnt. 3.045 m^3

(2) The calorific power of the gas per cubic meter. 1633 Calories.

(3) The proportion of the calorific power of the fuel obtainable on burning the gas. 66.5 per cent.

(4) The proportion of the calorific power of the fuel which has been sacrificed in making the gas, assuming it burnt cold. 33.5 per cent.

Problem 41.

Producer gas of the following composition:

Carbon monoxide	28 per cent.
Carbon dioxide	4 "
Hydrogen	4 "
Methane	2 "
Water vapor	1 "
Nitrogen	61 "

is burned with 10 per cent. more air than theoretically required, both air and gas being preheated to 1000° C.

Required: The theoretical maximum temperature of the flame. 2100° C.

Problem 42.

Kiln-dried peat from Livonia contained by analysis:

Carbon	49.70 per cent.
Hydrogen	5.33 "
Oxygen	30.76 "
Nitrogen	1.01 "
Ash	13.23 "

The wet peat, as taken from the ground, carried 75 per cent. of water, when air-dried 20 per cent., and when kiln-dried none, as per analysis.

The air-dried peat is dried in a kiln by means of a current of hot air, which enters the kiln, and comes in contact with the freshly-charged peat, at a temperature of 150° C., while it leaves the kiln, near the discharge end, at 50° C. Outside temperature 0° C., outside air dry. The kiln loses by radiation 10 per cent. of the sensible heat of the hot air coming into it, the rest represents the sensible heat of the warm moist air and

dried peat, issuing at 50° C., and the heat necessary to evaporate the moisture. The air required is heated in a stove where kiln-dried peat is burned, 75 per cent. of the heat generated being transferred to the air. Mean specific heat of kiln-dried peat 0.25.

Required: (1) The practical calorific powers of wet peat, air dried peat and kiln dried peat. 607; 3278; 4249.

(2) The volume of air, at standard conditions, needed for drying one metric ton of air-dried peat. 5,122 m^3.

(3) The percentage degree of saturation, with moisture, of the issuing air. 35.4.

(4) The amount of kiln-dried peat required to be burned in the stove per ton of air-dried peat put through the kiln, and the percentage of the total fuel necessary for this purpose. 70.5 kg. 9.25%.

Problem 43.

A set of four coke ovens produce 10,000 cubic feet of gas per hour, measured at 60° F., and having the composition H^2 64.3 per cent., CO 20.7, CH^4 5.4, C^2H^4 0.5, C^6H^6 0.5, CO^2 2.0, O^2 1.0, N^2 5.6 per cent. Temperature leaving the ovens 2900° F. For half of each hour the whole gas is burned by the theoretical amount of cold air, as it passes into recuperators, whence the products at 1900° F. pass under steam boilers where their temperature is reduced to 500° before passing to the stack. For the second half of each hour the gases pass through the recuperators unmixed with air, are there heated to 1900° F., and at that temperature pass under boilers where they meet with the theoretical quantity of air needed for combustion, are burned, and the products pass to the stack at 500° F.

Required: (1) The horse-power of the boilers during the first 30 minutes, calling 1 horse-power the ability to evaporate 34½ pounds of water per hour at 212° F., and assuming the boilers to produce steam representing 50 per cent. of all the heat received by them and generated within them (net efficiency 50 per cent.). 23.4 H. P.

(2) The same, for the second 30 minutes. 57.0 H. P.

Problem 44.

A plant of by-product coke ovens uses bituminous coal containing 76 per cent. of carbon, and having a calorific power

of 9000, produces coke containing an average of 86 per cent. of carbon, and having a calorific power of 7000, while the by-product tar produced contains 20 per cent. of carbon. The coke weighs 70 per cent. and the tar 5 per cent. of the weight of the coal used. The average analysis of the gases for the month of January, 1904 (samples dried before analysis) was:

Carbon dioxide	3.00	per cent.
Oxygen	0.50	"
Carbon monoxide	5.10	"
Marsh gas, CH^4	35.00	"
Illuminants C^2H^4	2.13	"
Illuminants C^3H^8	1.06	"
Illuminants C^6H^6	1.06	"
Hydrogen	40.00	"
Nitrogen	12.15	"

Required: (1) The volume of by-product gases, at standard barometric pressure and at 60° F., produced per ton (2000 pounds) of coal used. 16,294 cubic feet.

(2) The proportion of the calorific power of the coal represented by the calorific powers of the coke and the gases. 54.4%; 27.4%.

(3) Using half the gases produced in gas-engines, at an efficiency of conversion into power of 25 per cent., how many horse-power-hours could be thus generated per pound of coal coked? 0.22 H. P. hours.

Problem 45.

A gas producer uses coal which analyzed: total carbon 75.68 per cent., oxygen 12.70 per cent., hydrogen 4.50 per cent., ash 7.12 per cent. The ashes produced contain 21.07 per cent. of unburnt carbon. The gas carried 30.4 grams of moisture to each cubic meter of dried gas collected, and the latter shows on analysis:

Carbon dioxide	5.7	per cent.
Carbon monoxide	22.0	"
Methane (CH^4)	2.6	"
Ethylene (C^2H^4)	0.6	"
Hydrogen	10.5	"
Oxygen	0.4	"
Nitrogen	58.2	"

A steam blower furnishes blast, forcing in the outside air which carries 15 grams of moisture per cubic meter, measured dry at 20° C.

Required: (1) The volume of gas (dry) produced per kilo. of coal used. 4.337 m^3.

(2) The weight of steam used by the blower per kilo. of coal used. 0.2691 kg.

(3) The weight and volume of air blown in, per kilo. of steam used by the blower. 15.5 kg.; 12.95 m^3.

(4) The percentage of the steam blown in which is not decomposed in the producer, assuming the moisture in the gas to represent steam used and not decomposed (assumption not strictly accurate). 49.3%.

(5) The mechanical efficiency of the blower, assuming it uses steam at 4 atmospheres effective pressure, and produces 10 centimeters of water gauge pressure in the ash pit of the producer. 4.67%.

Problem 46.

Assume the gas of Problem 42 to be produced by the combustion of 1000 kilos. of coal per hour in the producers, and to be burned in a furnace with such excess of air (carrying at 20° C. 15 grams of moisture per cubic meter measured dry) that the chimney gas, analyzed dry, contains:

Carbon dioxide	12.7 per cent.
Nitrogen	80.6 "
Oxygen	6.7 "

These products of combustion enter the chimney at 500° C. and leave it at 350° C., their velocity entering at the base is 4 meters per second. Outside air 20°. The efficient draft is 2.5 centimeters of water gauge, measured at the base; assume this 90 per cent. of the total head of the chimney.

Required: (1) The diameter of the chimney, assuming it round, and its height, assuming its section uniform. 1.52 meters; 41.3 meters.

(2) The work done by the chimney, expressed in horse-power. 2.6

(3) The energy efficiency of the chimney, *i.e.*, the ratio of the mechanical work it performs to the mechanical equivalent of the heat which it receives. 0.079 per cent.

Problem 47.

Assume the chimney of Problem 46 to be built of fire-brick of an average thickness of 60 centimeters; that the gases passing through per hour are 1586 cubic meters of nitrogen and air, 315 cubic meters of carbon dioxide and 234 cubic meters of water vapor; the temperature at the base is 500° C., at the top 350°; the velocity of the hot gases at the base, 4 meters per second; diameter 1.52 meters, height 41.3 meters. Assume further the coefficient of transfer of heat from gas to brick and brick to air to be $\frac{2+100\sqrt{v}}{36{,}000}$ (in C. G. S. units), and the velocity of the wind outside to be 20 kilometers per hour.

Required: The coefficient of conductivity of the fire-brick in C. G. S. units. 0.31

PART II.

IRON AND STEEL.

CHAPTER I.

BALANCE SHEET OF THE BLAST FURNACE.

As the most important factor in the production of the most important metal, the blast furnace is the most important furnace or piece of metallurgical apparatus in the world. It is, therefore, proper that we should commence a series of articles on the application of metallurgical principles and calculations to the metallurgy of iron, by a discussion of the blast furnace; and since this discussion, to be complete, must include a wide range of topics, we will commence with the simplest, viz.: the balance sheet of materials, entering and leaving the furnace. Later we can discuss the balance sheet of heat entering in, developed within and leaving the furnace, the reactions taking place in the furnace, the action of hot and of dried blast, the calculation of the proper constituents of the charge, the temperatures attained before the tuyeres, unused combustible energy of the gases, efficiency of the hot-blast stoves, and other interesting and practically valuable factors in the running of the furnace.

The blast furnace may be regarded from several points of view; we will mention two. First, it may be regarded as a huge gas producer, run by hot, forced blast, in which the incombustible portions of the contents are melted down (with a little unburnt carbon) to liquid metal and slag, and are run out beneath, while the gaseous products pass upwards through 50 to 100 feet of burden, and escape above. The escaping gases are primarily of the composition of producer gas, with some of its carbonous oxide changed to CO^2 by the oxygen abstracted from the burden, with some CO^2 added from the decomposition of the carbonates of the charge, and with the usual increment of moisture from the charge and volatile matter (if any) from the distillation of the fuel. From this point of view, the blast furnace is a huge gas producer, giving a rather inferior quality of combustible gas in very large quantities, and incidentally

reducing to metal and slag the burden of iron ore and flux (limestone) which is put in with the fuel. The treatment of the furnace as a metallurgical problem may then proceed as the discussion of a gas producer, with the composition of the gas produced somewhat modified by the amount of oxygen given up to the gas by the reducible portions of the charge of the furnace.

The other viewpoint is to regard the furnace as primarily an apparatus for deoxidizing or reducing iron ore, for which purpose the ore is charged with sufficient carbonaceous fuel to do two things, viz.: to abstract all the oxygen from the reducible metallic oxides, and to furnish enough heat, or high enough temperature, to melt down to superheated liquids the pig iron and slag (combinations of irreducible metallic oxides) formed. In this view, the fuel must supply the reducing energy and the melting-down or smelting requirements; the first by acting upon the metallic oxides at a red to a white heat and abstracting their oxygen; the second, by being burned at the foot of the furnace by hot air blast, and there generating the heat and higher temperatures necessary for the smelting down of the already reduced materials.

Materials Charged and Discharged.

The materials put into a blast furnace may all be classed under four heads:

Fuel..... } Charged at the throat.
Iron ore..... }
Fluxes..... }
Blast..... Blown in at the tuyeres.

The materials discharged from the furnace may be classed under four heads also:

Pig iron..... } Tapped from the crucible.
Slag..... }
Gases..... } Passing out at the top.
Dust..... }

We will discuss the resolution of each of the four materials charged into the four avenues of escape.

Fuel.

The fuel used is sometimes charcoal, but in the great majority of cases coke, with perhaps some raw bituminous coal

or anthracite coal, or in a few cases all raw bituminous coal. The composition of these fuels consists of moisture, volatile matter, fixed carbon, sulphur and ash consisting of silica, lime, iron, alumina, alkalies, etc.

The moisture is driven off near the top, and goes into the gases as moisture. The volatile matter is expelled near to the top; almost all of it goes unchanged into the gases, but part of the hydrocarbons thus expelled may be decomposed and deposit fixed carbon on the iron oxides, etc., surrounding them. This carbon, however, will take up oxygen from the charge lower down in the furnace, and thus eventually pass into the gases as CO or CO^2. We can, therefore, assume without error that all the volatile constituents of the fuel pass into the gases, but cannot be certain in exactly what state of combination, except as regards the moisture. It will be quite exact if we know the ultimate composition of the volatile matters of the coal, as so much carbon, hydrogen, oxygen, nitrogen, sulphur, etc., to charge them thus entirely to the gases.

The fixed carbon all finds its way ultimately into the dust or the gases, either as CO, CO^2, CH^4 or HCN, or alkali cyanides, excepting the amount represented by the carbon in the pig iron. Subtracting the carbon in the pig iron from the total fixed carbon in the fuel, the difference can safely be put down as entering the gases or being in the dust carried away by the gases.

The sulphur in the fuel has a more varied history. When it is partly present in the form of iron pyrites, some may go into the gases as sulphur vapor, and eventually be burned to SO^2 when the gases are burned; another part may be oxidized in the furnace itself to SO^2, and as such appear in the gases; the rest, along with organic sulphur, passes either into the slag or the pig iron. Sulphur passing into the slag seems to do so as calcium sulphide, CaS, formed by some such reaction as

$$CaO + C + FeS = CaS + CO + Fe$$

or, if the sulphur was present in the fuel as gypsum,

$$CaSO^4 + 4C = CaS + 4CO$$

The amount of sulphur going into the iron depends really upon

the opportunity for it to go into the slag. If the temperature of the furnace at the tuyeres is very high, and especially if the slag is low in silica, sulphur will keep out of the iron and go into the slag, to the extent of ten or twenty times as much being in the slag as in the iron; but if the temperature is low and the slag rich in silica the reverse may be the case. A high temperature and a high percentage of lime in the slag are the blast furnace manager's means of keeping down the sulphur in the iron, although high magnesia or high alumina are also efficacious. In casting up the balance sheet it can be assumed that when using coke or charcoal all the sulphur of the fuel goes either into the slag or the iron, and knowing from the analysis of the pig iron made how much goes into it, the rest can be calculated as going into the slag as CaS. If raw coal is used, it is uncertain how much sulphur goes into the gases, and an exact analysis of either the slag or gases, for sulphur, in addition to that of the pig iron, would be necessary to fix its distribution.

The ash of the fuel counts in with the other incombustible ingredients of the charge. Some of the silica in it may be reduced to silicon, and some of the CaO to Ca, to form CaS; while most of the iron will pass into the pig iron. It is in most cases uncertain whether the silicon in the pig iron comes at all from the fuel ash, so it is usual to assume it as coming from the silica of the ore only; as to the iron, it is best to assume it all reduced to the metallic state, as is probably always the case.

Besides all these avenues of escape for the constituents of the fuel, it is sometimes necessary to take into account the possibility of some of it, in fine particles, being carried out of the furnace bodily with the outgoing gases. If the amount of this in the dust is determined, it must be subtracted *in toto* from the fuel charged, and then the remainder distributed as just discussed.

Illustration.—A blast furnace is charged, per 1,000 kilos. of pig iron produced, with 925 kilos. of coke, containing by analysis: Fixed carbon, 86 per cent.; volatile carbon, 2; hydrogen, 1; oxygen, 0.5; nitrogen, 0.5; sulphur, 1.0; iron, 2; silica, 5; lime, 1; moisture, 1. The pig iron contains 3.5 per cent. of carbon and 0.1 per cent. of sulphur. The dust carries 15 kilos. of dry

coke per metric ton of pig iron. Required the distribution of the coke in the furnace per ton of pig iron made:

Charges.		Pig Iron.	Slag.	Gases.	Dust.
Coke.....	925.0 kg.				
Dust.....	15.0 "	....	....	....	Coke 15.0
Fixed C.....	782.6 "	C 35.0	....	C 747.6	....
Volatile C....	18.2 "	....	....	C 18.2	....
H.....	9.1 "	....	....	H 9.1	....
O.....	4.5 "	....	....	O 4.5	....
N.....	4.5 "	....	....	N 4.5	....
S.....	9.1 "	S 1.0	S 8.1	....	....
Fe.....	18.2 "	Fe 18.2	....	....	....
SiO^2.....	45.5 "	....	SiO^2 45.5	....	....
CaO.....	9.1 "	....	CaO 9.1	....	....
H^2O.....	9.3 "	....	....	H^2O 9.3	....

ORE.

Whatever the varieties of ore used they can be averaged together, so as to get the average composition of the ore charged. Then, knowing its weight per unit of pig iron made, the distribution into pig iron, slag, gases and dust can be made.

There may, first of all, be blown out as ore dust up to 25 per cent. of the ore charged. This must be first deducted as dry ore and then the rest distributed to pig iron, slag and gases.

The moisture of the ore, also any carbonic acid, may be considered as going over bodily into the gases. The sulphur may partly go into the gases if present as iron pyrites (this amount would have to be checked by an analysis of the gases for sulphur or hydrogen sulphide), but mostly into the slag as CaS. Some of it may be put down as going into the pig iron, if the sulphur in the fuel does not account for all that appears in the analysis of the iron. The iron oxides present must be assumed reduced to metallic iron sufficient to furnish the iron in the pig iron from its analysis; the excess, if any, if put down as going into the slag as FeO; all the oxygen given off (the difference between the weight of iron oxide in the ore and the sum of iron going in the pig iron and ferrous oxide passing in the slag) goes to the gases. If there is not enough iron in the ore to account for all in the pig iron, then none is assumed to go into the slag.

The manganese oxides in the ore furnish the manganese in the pig iron, the excess going into the slag as manganous oxide MnO, the oxygen (by difference) goes to the gases. The proportion of manganese reduced to metal increases with the temperature at which the furnace is run and as the slag is less siliceous. The amount reduced is known, however, only by the analysis of the pig iron.

Zinc in the ore is partly found as ZnO in the slag, and partly as flakes of white zinc oxide in the gases, which latter partly deposit in the dust catcher and are partly carried by the current of gases into the stoves and under the boilers. The relative amounts going into slag and gases can be best controlled by analysis of the slag.

Copper, silver, gold, nickel, cobalt, phosphorous, antimony and arsenic are almost completely reduced into the pig iron; careful analysis of the latter will show exactly to what extent, but without this careful analysis they may be assumed to pass completely into the iron. Lead is mostly carried out as fume, a small amount passes into the pig iron, and, if present in quantity, a large amount may collect as metallic lead beneath the pig iron and, if it can, soak into the foundation of the furnace.

Alumina usually passes completely, as such, into the slag. When present in large amount, producing a slag rich in alumina, and with very hot blast, the pig iron may contain as much as 1 per cent. of aluminium, the oxygen thereof passing into the gases. Magnesia may be assumed as passing completely into the slag; none is reduced. Lime goes into the slag, except a not-unimportant quantity which is reduced by carbon in the presence of sulphur compounds, and forms CaS, its oxygen passing into the gases; a very small amount may go as calcium into the pig iron. Alkaline metals partly go into the slag, while some may pass into the gases as alkaline cyanides. Titanium oxide, tungsten oxide, chromium oxide and the oxides of molybdenum, uranium, vanadium are sometimes reduced in small amounts, the more the hotter the furnace is run and the more basic the slag, while the bulk of them passes into the slag as the lowest oxide which each is capable of forming.

Silica mostly goes into the slag as SiO^2, but a portion is always reduced to silicon in the pig iron. The amount reduced is greater the hotter the furnace is run, the more slowly it is

run, and the more siliceous the slag. In some cases as much as one-quarter of all the silica going into a furnace is reduced to silicon. It is probably reduced only by carbon dissolved in iron at the lower part of the furnace. The oxygen of the silica reduced goes into the gases.

Illustration.—1956.8 kilograms of ore is charged into a furnace per metric ton of pig iron made. The ore analyses: Fe^2O^3, 71.43 per cent.; SiO^2, 14.24; CaO, 2.05; MgO, 1.51; MnO^2, 4.15; SO^3, 1.40; H^2O, 5.00; Cu^2O, 0.22 per cent. The pig iron contains 93.03 per cent. iron, 3.27 carbon, 1.20 manganese, 0.08 sulphur, 0.40 copper, 2.02 silicon. Assume the dry ore dust to weigh 4 per cent. of the weight of ore charged, and that there is no sulphur found in the gases, but all the sulphur in the pig iron comes from the fuel. Cast up the distribution of the ore:

Charge.		*Pig Iron.*	*Slag.*	*Gases.*	*Dust.*
Ore.....	1956.8 kg.				
Dust.....	78.1 "	....	....	....	Ore 78.1
Fe^2O^3.....	1339.2 "	Fe 930.3	FeO 9.1	O 499.8	....
SiO^2.....	267.0 "	Si 20.2	SiO^2 223.6	O 22.2	....
MnO^2.....	77.8 "	Mn 12.0	MnO 48.0	O 17.8	....
Cu^2O.....	4.1 "	Cu 3.6	....	O 0.5	....
CaO.....	38.4 "	....	CaO 20.1 Ca 13.1	O 5.2	....
MgO.....	28.3 "	....	MgO 28.3	....	....
SO^3.....	26.3 "	....	S 10.5	O 15.8	....
H^2O.....	97.6 "	....	....	H^2O 97.6	....

In calculating the above we note that the dust is dry, and weighs 4 per cent. of the ore, making 78.1 kilos. of dry dust, representing 82 kilos. of moist ore, leaving 1874.8 kilos. of moist ore to be distributed, plus the 3.9 kilos. of water from the dust, which also goes into the gases. This 1874.8 kilos. contains the weights given, calculating from its analysis. The 1339.2 kilos. of Fe^2O^3 contains 937.3 kilos. of iron; but there are only 930.3 kilos. in the ton of pig iron, therefore the other 7.0 kilos. must go into the slag as $7.0 \times \frac{72}{56} = 9.1$ kilos. of ferrous oxide, while $1339.2 - (930.3 + 9.1) = 499.8$, the weight of oxygen

going into the gases. The 267.0 kilos. of silica contains 124.6 kilos. of silicon, but there are only 20.2 kilos. in the pig iron, therefore, 104.4 kilos. must remain unreduced, passing into the slag as $104.4 \times \frac{60}{28} = 223.6$ kilos. of silica, while $267 - (20.2 + 223.6) = 22.2$ kilos. of oxygen goes into the gases. Another, and equally logical procedure, is to start with the 20.2 kilos. of silicon in the pig iron, which must have required $20.2 \times \frac{60}{28} = 42.4$ kilos. of silica to furnish it, yielding $42.4 - 20.2 = 22.2$ kilos. of oxygen to the gases, and leaving $267.0 - 42.4 = 223.6$ kilos. of silica unreduced to go into the slag.

The 12.0 kilos. of manganese in the pig iron would be reduced from $12.0 \times \frac{87}{55} = 19.0$ kilos. of MnO^2, furnishing, therefore, 7.0 kilos. of oxygen to the gases, and leaving $77.8 - 19.0 = 58.8$ kilos. of MnO^2 to go into the slag as MnO. The molecular weights of MnO and MnO^2 being respectively 71 and 87, there is $58.8 \times \frac{71}{87} = 48.0$ kilos. of MnO going into the slag, while 10.8 kilos. more of oxygen will be supplied to the gases, making altogether $10.8 + 7 = 17.8$ kilos. of oxygen given up by the MnO^2. The 4.1 kilos. of Cu^2O contain 3.6 kilos. of copper, all of which enters the pig iron and contributing 0.5 kilos, of oxygen to the slag.

The 38.4 kilos, of CaO must supply enough Ca to form CaS with the S of the SO^3. The latter quantity is $26.3 \times \frac{32}{80} = 10.5$ kilos., to supply which there is needed $10.5 \times \frac{40}{32} = 13.1$ kilos. of calcium. The latter will be supplied by $13.1 \times \frac{56}{40} = 18.3$ kilos. of CaO, furnishing 5.2 kilos. of oxygen to the gases, and leaving $38.4 - 18.3 = 20.1$ kilos. of CaO unreduced to go into the slag. The MgO in the ore goes directly into the slag. The oxygen of the SO^3 goes into the gases. The 5 per cent. of

water of the whole quantity of ore charged goes into the gases. as vapor.

Flux.

The flux is used for the purpose of making a fusible slag with the slag-forming ingredients, contributed by the ore and fuel. If we consider the distribution of ore and fuel given in the preceding illustrations we see that the chief material to be fluxed is silica, with smaller quantities of FeO, MnO, CaO, MgO and CaS. The cheapest and most available material to flux silica is limestone, the slag formed being a silicate of lime, magnesia and alumina, with CaS and smaller quantities of other basic oxides. We will not discuss at present the considerations governing the amount of flux used, since this is a calculation requiring separate treatment, as the proper working of the furnace depends fundamentally upon it. We may remark here that enough flux must be used to make an easily fusible fluid slag, rich enough in lime, magnesia or alumina to carry away satisfactorily the bulk of the sulphur, and so produce good pig iron.

The flux usually contains CaO, MgO, Al^2O^3, SiO^2, FeO, CO_2 and H^2O. Its H^2O and CO^2 are driven off in the upper third of the furnace, and may be put down as going as such into the gases. The FeO may be reduced if the slag is very clean, but under ordinary conditions may be put down as all going into the slag, unless in quite large amount, because the iron in ore and fuel usually supplies the total weight of iron in the pig iron. The silica and alumina may be carried over bodily into the slag. The magnesia can be put at once into the slag, but the lime cannot in many cases be treated that way, because quite frequently some is needed to supply calcium for the sulphur of the fuel. In the fuel previously illustrated, for instance, there is not enough CaO present to furnish Ca for the S, whence it follows that some CaO from the flux will be needed to make up the deficit. We may, in such a case, either consider all the CaO of the fuel to form CaS with part of the sulphur, and then take enough CaO from the flux to unite with the remainder, or, it is equally permissible to take all the CaO necessary to furnish Ca to all the sulphur of the fuel, and to let the CaO of the fuel figure as passing entirely into the slag. The latter requires a little less calculation.

Illustration.—A blast furnace receives 503 kilos. of limestone flux per metric ton of pig iron made, which analyses CaO, 29.68 per cent.; MgO, 20.95; SiO^2, 3.07; Al^2O^3, 2.66; FeO, 0.48; CO^2, 42.66; H^2O, 0.50 per cent. Assume 8.1 kilos. of sulphur in the fuel, for which the flux must provide calcium. Required the distribution of the flux, assuming it to make no dust:

Charge.		*Pig Iron.*	*Slag.*		*Gases.*	
Flux	503.0 kg.	....				
CaO	149.3 "	....	Ca	10.1	O	4.1
			CaO	135.1		
MgO	105.4 "	....	MgO	105.4	....	
SiO^2	15.4 "	....	SiO^2	15.4	....	
Al^2O^3	13.4 "	....	Al^2O^3	13.4	....	
FeO	2.4 "	....	FeO	2.4	....	
CO^2	214.6 "	....	.....		CO^2	214.6
H^2O	2.5 "	....	.....		H^2O	2.5

The only calculation needed above is that 8.1 kilos. of sulphur require $8.1 \times \frac{40}{56} = 10.1$ kilos. of calcium, which would be furnished by $10.1 \times \frac{32}{40} = 14.2$ kilos. of lime, leaving 4.1 kilos. of oxygen to go into the gases and 135.1 of lime to go into the slag.

Blast.

The remaining item needed to complete the balance sheet is the amount of blast. This may be roughly estimated by obtaining the piston displacement of the blowing engines, and assuming a coefficient of delivery into the furnace. This is very rough, because the efficiency is not known, and may vary anywhere between 0.5 and 0.95. Another rough approximation may be obtained by observing the pressure of the blast, its temperature, the back pressure in the furnace, and knowing the area of the tuyeres, and assuming a coefficient of contraction of the hot air jet as it emerges from the tuyeres. Here, again, are several uncertain factors, and the coefficient may vary between 0.9 and 0.98. Calculations on this basis are very rough.

The only satisfactory way to determine the blast is to carefully analyze the gases, determining carefully all the carbon, oxygen and nitrogen which they contain. Since the carbon comes only from the charges, the amount of gases produced per unit of pig iron made becomes known, and thence the oxygen and nitrogen contained in them. These, minus the oxygen and nitrogen coming from the solid charges, leave the oxygen and nitrogen which must have come from the blast. The oxygen in the blast, minus $\frac{3}{10}$ the nitrogen, gives the oxygen entering as water vapor; but this last calculation is not so satisfactory as to observe the atmospheric conditions, and calculate the air and moisture on the basis of the contained nitrogen.

The blast contains oxygen, nitrogen and moisture. All its constituents pass into the gases, being put down as so much oxygen, nitrogen and hydrogen. Just how much of that hydrogen gets into the gases as free hydrogen and how much as water vapor is not known. Argon and other rare gases in the blast are counted and treated as nitrogen. The carbonic acid of the air is present relatively in such a small amount that it can be neglected, as far as all ordinary calculations are concerned.

Problem 51.

A blast furnace at Herrang, Sweden, is run on ore briquettes made by pressing and calcining fine concentrates. The analyses of briquettes, charcoal and limestone flux are as follows (see Journal Iron and Steel Institute, I., 1904):

	Briquettes.	*Limestone.*	*Charcoal.*
Fe^2O^3	85.93	0.18	0.32
FeO	3.96	....	C 80.31
SiO^2	5.50	3.14	0.19
MnO	0.63	....	N 0.08
Al^2O^3	0.76	0.32	O 3.54
CaO	2.23	53.74	0.89
MgO	0.97	0.17	0.10
P^2O^5	0.006	0.006	0.0068
S	0.010	0.001	0.017
Cu	0.007	CO^2 42.42	H^2O 14.04
			K^2O 0.50

The pig iron contains phosphorus, 0.012 per cent.; sulphur, 0.007; manganese, 0.025; silicon, 0.60; carbon, 2.70; iron, 96.656. There is used in charging the furnace:

Briquettes	1,190 pounds
Limestone	.90 "
Charcoal	530 "

And the fuel consumption is 682 pounds of charcoal per 1,000 pounds of pig iron made.

The gases at the throat (dried) analyze: N^2, 57.3 per cent.; CO, 23.1; CO^2, 14.8; H^2, 4.3; CH^4, 0.5 (Rinman). Assume blast dry. Dust in gases neglected.

Required: (1) A balance sheet of materials entering and leaving the furnace, per 1,000 pounds of pig iron made. (2) The percentages of iron, manganese, silicon, sulphur and phosphorus going into the furnace, which go into the pig iron.

Solution:—(1) See table opposite page.

(2) The total iron in the charge is 969.2 kilos., while that in the pig iron is 966.6; the efficiency of the reduction of iron is therefore 99.7 per cent.

The total manganese in the charge is $9.6 \times \frac{55}{71} = 7.4$ kilos., of which only 0.25 gets into the pig iron, or 3.4 per cent.

The total silica charged is 89.1 kilos., representing 41.6 kilos. of silicon, of which 6.0 kilos. enters the pig iron, or 14.4 per cent.

The sulphur charged is 0.270 kilos., of which the pig iron contains 0.07, or 25.9 per cent.

The phosphorus charged is 0.063 kilos., while the analysis of the pig iron shows in it 0.12 kilos. It is thus evident that all the phosphorus goes into the pig iron; for while the analysis shows more phosphorus in the pig iron than was put into the furnace, yet the divergence is evidently due to segregation or concentration of phosphorus in the sample taken, and the practical conclusion is that all the phosphorus in the charge finds its way into the pig iron.

Notes on the Balance Sheet.

The Fe^2O^3 of the ore is assumed all reduced, because the 920.4 kilos. of iron in it is less than the 966.6 kilos. of iron known to be in the 1,000 kilos. of pig iron from its analysis.

Solution.— (1)

BALANCE SHEET (PER 1000 OF PIG IRON).

Charges		*Pig Iron*		*Slag*		*Gases*	
Ore	1530.2						
Fe^2O^3	1314.9	Fe	920.4	.....		O	394.5
FeO	60.6	Fe	46.2	FeO	1.2	O	13.2
SiO^2	84.2	Si	6.0	SiO^2	69.6	O	8.6
MnO	9.6	Mn	0.25	MnO	9.3	O	0.1
Al^2O^3	11.6		.....	Al^2O^3	11.6		.....
CaO	34.1		.....	CaO	34.1	O	0.03
MgO	14.8		.....	MgO	14.8		....
P^2O^5	0.092	P	0.04	.....		O	0.05
S	0.153	S	0.07	CaS	0.19		....
Cu	0.11	Cu	0.11	.....		O	0.01
Limestone	115.8						
Fe^2O^3	0.2		.....	FeO	0.2	O	0.02
SiO^2	3.6		.....	SiO^2	3.6		....
Al^2O^3	0.4		.....	Al^2O^3	0.4		....
CaO	62.2		.....	CaO	62.2		....
MgO	0.2			MgO	0.2		....
P^2O^5	0.007	P	0.003	.....		O	0.00
S	0.001		.....	CaS	0.0		....
CO^2	49.1		.....	.....		CO^2	49.1
Charcoal	682.0						
C	547.7	C	27.0	.....		C	520.7
N	0.5		.....	.....		N	0.5
O	24.1		.....	....		O	24.1
Fe^2O^3	2.2		.....	FeO	2.0	O	0.2
SiO^2	1.3		.....	SiO^2	1.3		....
CaO	6.1		.....	CaO	5.9	O	0.06
MgO	0.7		.....	MgO	0.7		....
P^2O^5	0.046	P	0.02	.....		O	0.03
S	0.116		.....	CaS	0.25		....
K^2O	3.4		.....	K^2O	3.4		....
H^2O	95.8		.....	.....		H^2O	95.8
Blast	2416.8						
O^2	557.7		.....	.....		O	557.7
N^2	1859.1		.....	.....		N^2	1859.1
Totals	4744.0		1000.0		220.8		3543.7

The FeO, however, cannot be assumed all reduced, because it would furnish 47.1 kilos. of iron, and there is only 966.6—920.4 = 46.2 kilos. of iron yet to be supplied. We, therefore, put down 46.2 kilos. of iron as going to the pig iron, thus furnishing all the iron in the pig iron, and leaving 0.9 kilos. of iron to go over into the slag as 1.2 kilos. of FeO. Having thus allowed for all the iron in the pig iron, the Fe^2O^3 in the limestone and fuel must be assumed as passing entirely into the slag as FeO.

The 6 kilos. of silicon in the pig iron is put down as coming entirely from the SiO^2 of the ore, of which 14.6 kilos. is thus used up, leaving 15.6 kilos. to go into the slag. The SiO^2 of flux and fuel must then be regarded as passing entirely into the slag.

The 0.25 of manganese in the pig iron comes from the MnO of the ore, requiring 0.35 of MnO, and leaving 9.3 of MnO to go into the slag.

The Al^2O^3 and MgO of ore, flux and fuel go bodily into the slag.

The sulphur in the ore, 0.153 kilos., is more than enough to supply the 0.07 kilos in the pig iron. We, therefore, put down 0.07 kilos. as going into the pig iron, supplying all the latter contains, and calculate the remaining 0.083 kilos. to CaS going into the slag. The CaO necessary to furnish this calcium is 56 for every 32 of sulphur (CaO = 56, S = 32), or 0.14 kilos., which, therefore, must be deducted from the 34.1 kilos. of CaO present in the ore. The oxygen of this 0.14 kilos. of CaO finds its way into the gases.

The 0.092 kilos. of P^2O^5 present in the ore contain only 0.04 kilos. of phosphorus, and since the pig iron contains, from its analysis, 0.12 kilos., we may assume all of this going into the pig iron. The same remarks are true of the P^2O^5 in flux and fuel; altogether, they come somewhat short of supplying all the phosphorus in the pig iron, and are, therefore, considered as completely reduced. The copper goes entirely into the pig iron, although not given in the analysis.

The Fe^2O^3 of the limestone must be transferred entirely as FeO to the slag, since all the iron needed for the pig iron has been already provided. The same is true of the Fe^2O^3 of the fuel; and an analogous statement applies to the SiO^2 and sul-

phur of both flux and fuel. The sulphur of the fuel does not produce an amount of CaS which counts in significant figures, and the CaO required is likewise insignificant, as is also the oxygen thus furnished the gases. In such cases, instead of ignoring the item altogether, or putting down wholly insignificant quantities, the amounts are expressed as 0 00, denoting no significant amount.

The fixed carbon of the fuel, only, furnishes the carbon in the pig iron, the rest going into the gases. The blast is calculated as follows:

Carbon in CO^2 of flux $= 49.1 \times \frac{12}{44}$ = 13.39 kilos.

Carbon in gases from fuel = 520.70 "

Carbon in gases altogether = 534.09 "

Carbon in 1 cu. meter of gas $(0.231 + 0.148 + 0.005) \times 0.54$ = 0.20736 "

Volume of gas per 1,000 of pig iron $534.09 \div 0.20736$ = 2575.6 m^3

Nitrogen in this gas 2575.6×0.573 = 1475.9 "

Weight of nitrogen 1475.9×1.26. = 1859.6 kg.

Nitrogen from fuel = 0.5 "

Nitrogen from blast..... = 1859.1 "

Oxygen from blast 1859.1×0.3..... = 557.7 "

CHAPTER II.

CALCULATION OF THE CHARGE OF THE BLAST FURNACE.

In the last chapter we discussed the balance sheet of materials entering and leaving the furnace, showing the distribution of the ingredients of the charge and the blast into the various products and by-products of the furnace. We did not there go into the question as to how the proportions of the charge are determined by the metallurgist in charge of the furnace. There are, however, very few factors of the charge which can be controlled at will. The blast furnace reduces practically all of the iron present in the ore into the pig iron, and, therefore, if the ore contains 50 per cent. of metallic iron and the pig iron 90 per cent., it will take $0.90 \div 0.50 = 180$ parts of ore to furnish the iron in 100 parts of pig iron. The amount of ore to be used per unit of pig iron made is therefore fixed by the richness or poverty of the ore, and is not capable of variation. The amount of fuel used per unit of pig iron made is not fixed *a priori*, as is the amount of ore, but is governed by the calorific requirements of the furnace while in operation. If the pig iron and slag run colder than they should, it is evident that more heat must be put in or developed within the furnace, which the manager promptly proceeds to accomplish by increasing the temperature of the air blast (if he can), or by relatively increasing the amount of fuel in the charge (which he always can). The ratio of the weight of the ore and flux in the charge to the weight of fuel used is called the burden of the furnace, and in practice it is usual to charge at one time a fixed weight of fuel, and to vary the burden according to the heat requirements of the furnace. Changing the burden is therefore only another expression for changing the relative amount of fuel used, and this is varied simply from observation of the temperatures of iron and slag and the conclusions therefrom as to whether the burden is too

heavy or unnecessarily light. The amount of blast used is another factor relatively fixed per unit of pig iron produced. Blow more blast, and more pig iron is produced; blow no blast (bank the furnace), and no pig iron is made; the ratio is not quite exact, but it is quite nearly true that, other conditions being equal, the output of pig iron is nearly proportional to the amount of blast blown. Variations in the temperatures of the blast produce important changes, which will be separately discussed.

The amount of flux used is really the one factor in which the manager has the greatest freedom of action. The amount of this indispensable substance used is determined by many factors, and can be varied between quite wide limits without fundamentally deranging the furnace. It is here a question of using sufficient flux in the charge to make with the unreduced constituents of ore and ash of the fuel a slag which shall be well-fused at the temperature of the furnace, shall carry off considerable sulphur, if much is present, and shall not corrode the lining of the furnace. These considerations are so important, and often so little understood, that we will discuss them more at length.

Calculation of the Flux and Slag.

From the balance sheet of problem 51 it will be seen that the metallurgist running the Swedish blast furnace at Herrang, used, per 1,000 of pig iron made, 1530.2 of ore, 115.8 of limestone flux, 682 of charcoal, and blew in 2416.8 parts by weight of blast. It may with safety be believed that the amount of charcoal used was the minimum which he found by experience necessary to keep his furnace at proper temperature; and most American blast furnace managers will wonder how he could get along with so little. The amount of ore used was the necessary proportion to furnish the iron. The amount of blast was probably all that could be gotten out of the blowing apparatus with which the furnace was provided. Finally, the amount of flux was that amount necessary to make a proper slag. Let us investigate the question as to how its amount was determined and the characteristics of the proper slag.

The ingredients of the slag produced in the case in question are, from the balance sheet:

	From Ore.	*From Flux.*	*From Fuel.*	*Total*
SiO^2.....	69.6	3.6	1.3	74.5
Al^2O^3.....	11.6	0.4	....	12.0
CaO.....	34.0	62.2	5.9	102.1
MgO.....	14.8	0.2	0.7	15.7
FeO.....	1.2	0.2	2.0	3.4
MnO.....	9.3	....	....	9.3
K^2O.....	....	....	3.4	3.4
CaS.....	0.2	....	0.25	0.45
	140.7	66.6	13.55	220.85

And the percentage composition of the slag:

SiO^2	= 33.73 per cent.	FeO	= 1.54 per cent.
Al^2O^3	= 5.43 "	MnO	= 4.21 "
CaO	= 26.23 "	K^2O	= 1.54 "
MgO	= 7.11 "	CaS	= 0.20 "

The crucial question now presents itself, " What guided the metallurgist in choosing the quantity of lime stone used, and in making a slag of the above composition? " The answer to this will develop the whole practice of fluxing.

Primarily, the fundamental guide in this matter is previous experience, as revealed in recorded analyses of slags which have worked properly. Such analyses have been made for a hundred years, and freely published; they show what compositions of slag have been found practicable and suitable in blast furnace practice. As reported by the chemists, the analyses show the varying percentages of SiO^2, Al^2O^3, CaO, MgO, FeO, MnO, etc., found in actual slags made in successful practice, and this information would be the metallurgist's guide in calculating the amount of flux to use to produce a good slag. On studying these analyses, we find that silica and lime are the predominating constituents of all blast furnace slags, the reason being that silica is the principal material to be fluxed, and that lime (from limestone) is the cheapest material which will flux it, and form a fusible slag.

Analyses of numerous blast furnace slags show the following variations of composition:

SiO^2	25 to 65 per cent.	FeO	0 to 6 per cent.
Al^2O^3	3 " 30 "	MnO	0 " 14 "
TiO^2	0 " 10 "	K^2O \ Na^2O /	0 " 3 "
CaO	12 " 50 "		
MgO	0 " 18 "	CaS	0 " 9 "

The above limits are not reached simultaneously by one and the same slag. The ordinary variations may be summarized as follows (according to Ledebur):

	SiO^2	Al^2O^3	$CaO + MgO$
Producing gray iron, using charcoal	45—65	10— 5	45—25
Producing gray iron, using coke	30—35	15—10	50—55
Producing white iron, using charcoal	45—50	10— 5	45—
Producing white iron, using coke	30—40	10— 5	60—55
Producing spiegeleisen, using coke	30	10	55—45

In the latter case there is present 5—15 per cent, of MnO.

Among these varied compositions, however, there are various degrees of fusibility, and of suitability to the blast furnace's needs. The most easily fusible slags are those (considering only the main ingredients) which contain 35 per cent. of lime, and in which, if alumina is present, each 1 per cent. of alumina is balanced by the presence of 0.5 per cent. additional lime. This rule gives good slags up to about 65 per cent. of lime and alumina counted together. Another observation is, that with 33 to 40 per cent. of lime in the slag, the amount of silica and alumina together being some 60 to 70 per cent., it is possible to change the relations of silica to alumina within large limits (*i.e.*, from 40 to 50 silica and 20 alumina to 25 or 35 silica and 35 alumina) with very little effect upon the fusibility of the slag. On the other hand, with a low proportion of silica in the slag, say 30 to 40 per cent., it is equally possible to change the relations of lime to alumina within large limits (*i.e.*, from 50 lime and 15 alumina to 35 lime and 35 alumina) with very little effect upon the fusibility of the slag.

The blast furnace manager usually decides upon the kind of slag he will make, on one of three or four assumptions:

(1) If there is little alumina present, and practically no magnesia, he usually assumes some ratio between the weights of silica and lime which he desires his slag to possess, and calculates the weight of flux necessary to make slag conforming to that condition. In charcoal furnaces, where there is prac-

tically no sulphur in the charge, the silica may be 1.5 to 2.0 times the lime present; in coke furnaces, where it is necessary to eliminate much sulphur, this ratio is usually 0.5 to 1.0.

Illustration.—If a ton of iron ore carries 300 pounds of silica, how much limestone, which is practically pure calcium carbonate, will be required to slag it, neglecting flux necessary to slag the ash of the fuel?

Solution.—Pure limestone is $CaCO^3$, or $CaO \cdot CO^2$, and carries 56 per cent. of lime, which will go into the slag, and 44 per cent. of carbonic oxide (CO^2), which goes into the gases. Using x pounds of limestone, the weight of lime going into the slag is $0.56\,x$. If we assume the ratio of silica to lime = 1 for a coke furnace, and 1.75 for a charcoal furnace, we get the two equations and corresponding values of x:

$$\frac{300}{0.56\,x} = 1 \text{ whence } x = \underline{536} \text{ pounds.}$$

$$\frac{300}{0.56\,x} = 1.75 \text{ whence } x = \underline{307} \text{ "}$$

(2) If considerable magnesia is present it is usual to either count it simply as so much lime, or else to calculate the weight of lime to which it is chemically equivalent, and add this to the lime, calling the sum the " summated lime." The ratio of silica to lime is then used as the ratio of silica to lime plus magnesia, or of silica to summated lime. When there is considerable magnesia present the chemical summation should always be made. Small amounts of MnO, FeO and K^2O or Na^2O are also chemically summated as lime. The chemical summation is based on the fact that one molecule of a base containing one atom of oxygen is considered the equivalent in fluxing power of any other similar molecule; *e.g.*, CaO, MgO, FeO, MnO, K^2O, Na^2O are considered as equivalent; but as these molecules weigh differently, we have equivalent fluxing powers in the following weights:

CaO	56
MgO	40

FeO.....72
MnO.....71
K^2O.....94
Na^2O.....62

from which we conclude that since 40 parts by weight of magnesia is equivalent to 56 parts of lime, that, therefore, the lime equivalent of any weight of magnesia is $\frac{56}{40}$ of the weight of the magnesia. Similarly, we get the lime equivalent of these bases as follows:

CaO equivalent of any weight of MgO $= \frac{56}{40} \times$ weight MgO

" " " " FeO $= \frac{56}{72} \times$ " FeO

" " " " MnO $= \frac{56}{71} \times$ " MnO

" " " " $K^2O = \frac{56}{94} \times$ " K^2O

" " " " $Na^2O = \frac{56}{62} \times$ " Na^2O

Illustration.—An iron ore contributes to the slag 350 pounds of silica, 12 of FeO and 60 of MnO. It is desired to flux it by using limestone containing 38.1 per cent. lime, 13.6 magnesia, 3.4 silica, and 44.9 carbonic oxide (CO^2). How much flux must be used to produce a ratio of silica to summated lime = 0.8?

Solution.—Letting x be the pounds of limestone used, the ingredients of the slag will be

$SiO^2 = 350 + 0.034\,x$
$CaO = 0.381\,x$
$MgO = 0.136\,x$
$FeO = 12$
$MnO = 60$

The lime equivalents of the MgO, FeO and MnO are:

CaO equivalent of MgO $= 0.136\,x \times \frac{56}{40} = 0.1904\,x$

" " FeO $= 12 \times \frac{56}{72} = 9.33$

" " MnO $= 60 \times \frac{56}{71} = 47.32$

" " CaO $= 0.381\,x \times 1 = 0.381\,x$

Summated CaO $= 0.5714\,x + 56.65$

The ratio of silica to summated lime is therefore:

$$\frac{350 + 0.034\,x}{56.65 + 0.5714\,x} = 0.8$$

Whence $x = \underline{720}$ pounds.

It is easily seen that this method of solution, calling x the weight of flux used, and then getting expressions for the weight of each ingredient in the slag and the weight of the whole slag, is a very general solution which is applicable to any kind of assumed composition to which it is desired that the slag shall conform.

(3) If alumina is present in the slag-forming constituents of the ore it also may be reckoned with in several ways. It may be reckoned as so much by weight, and added in as such to the silica or the lime, or it may be calculated to its silica or its lime equivalent, and added into the summated silica or the summated lime. Here we touch on a question which has agitated blast furnace managers and theorists for a generation: Should the alumina be reckoned with the bases or with the acids; summated as silica or as lime? It would be presumptuous to set forth a dictum on a subject which has been so long and so ably discussed by some of the best iron metallurgists, but we will assume, as somewhere near the truth, that as far as the elimination of sulphur in the slag is concerned,

alumina acts in slags low in silica as though it were lime, not in the proportions of its lime equivalent

$$= \left(\frac{168}{102} \times \text{weight of alumina}\right)$$

but rather in about the proportions of its simple weight. As far as fusibility is concerned, in high silica slags alumina increases the fusibility up to a certain point, above which it decreases it. It acts in these, therefore, like lime, and may be classed with the bases. In low silica slags, below 45 per cent., alumina acts like silica when considerable is present, and like lime when less is present; for instance, in a low lime, high alumina slag, alumina and silica may be substituted one for the other within wide limits, without materially affecting the fusibility of the slag; in a high lime, high alumina slag, alumina and lime may be substituted for each other within wide limits without sensibly changing the fusibility. To state the matter as succinctly as possibe, in slags low in silica (30 to 35 per cent.), alumina reinforces the bases in the elimination of sulphur; in regard to fusibility, it acts like silica in a slag low in both silica and lime, and like lime in all other blast furnace slags.

Illustration.—An iron ore carries 10 per cent. of its weight of silica and 6 per cent. of alumina. The lime stone on hand contains 37.3 per cent. lime, 13.3 magnesia, 3.3 silica, 44 carbonic oxide (CO^2), and 2.1 per cent. alumina. How much flux is required per 1,000 parts of ore to make (*a*) a slag with 49 per cent. of silica plus alumina; (*b*) a slag with 33 per cent. silica; (*c*) a slag with summated silica = the summated lime?

Solution.

(*a*)

Weight of SiO^2 in slag	=	$100+0.033\,x$
Weight of Al^2O^3 in slag	=	$60+0.021\,x$
Weight of CaO in slag	=	$0.373\,x$
Weight of MgO in slag	=	$0.133\,x$
Total weight of slag	=	$160+0.560\,x$

therefore,

$$160+0.054\,x = 0.49\,(160+0.560\,x)$$

whence

$$x = \underline{370}$$

(*b*) $100+0.033\,x = 0.33\,(160+0.560\,x)$

whence

$$x = \underline{313}$$

(*c*)

Silica	$= 100$	$+0.033\,x$
Silica equivalent of alumina	$= \frac{180}{204}\,(60+0.021\,x)$	
Summated silica	$= 153$	$+0.0515\,x$
Lime	$=$	$0.373\,x$
Lime equivalent of magnesia	$= \frac{56}{40}$	$(0.133\,x)$
Summated lime	$=$	$0.5592\,x$

therefore $153+0.0515\,x = 0.5592\,x$

whence $x = \underline{300}$

Returning to the slag resulting from the proportions of flux chosen in Problem 51, and containing:

SiO^2	33.74 per cent.	FeO	1.54 per cent.
Al^2O^3	5.43 "	MnO	4.21 "
CaO	46.23 "	K^2O	1.54 "
MgO	7.11 "	CaS	0.20 "

We see that its percentage of silica is low, therefore it is adapted to produce pig iron low in sulphur; its percentage of alumina is low, and therefore its presence increases the fusibility of the slag, which would otherwise be rather deficient, because of the high lime and somewhat considerable amount of other bases. In such a slag, alumina would be summated with the bases.

The ratio of silica to bases is..... $\frac{33.74}{66.06} = 0.516$

The ratio of silica to lime plus magnesia is..... $\frac{33.74}{53.33} = 0.632$

The summated lime $= 46.23$

$+$CaO equivalent of $Al^2O^3 = \frac{168}{102}\,(5.43) = 8.94$

$$+\text{CaO equivalent of MgO} = \frac{56}{40}(7.11) = 9.95$$

$$+\text{CaO equivalent of FeO} = \frac{56}{72}(1.54) = 1.20$$

$$+\text{CaO equivalent of MnO} = \frac{56}{71}(4.21) = 3.32$$

$$+\text{CaO equivalent of } K^2O = \frac{56}{94}(1.54) = 0.92$$

$$\overline{70.56}$$

$$\text{Ratio silica to summated lime} = \frac{33.74}{70.56} = 0.478$$

Problem 52.

In a blast furnace charge, consisting of 1530.2 pounds of ore and 682 pounds of charcoal, per 1,000 pounds of pig iron made, it is known from the balance sheet of above materials that they will contribute to the slag the following slag-forming ingredients. (See balance sheet, Problem 51):

SiO^2	70.9 pounds.	FeO	3.2 pounds.
Al^2O^3	11.6 "	MnO	9.3 "
CaO	39.9 "	K^2O	3.4 "
MgO	15.5 "	CaS	0.4 "

The limestone at hand contains:

CaO	53.74 per cent.	Al^2O^3	0.32 per cent.
MgO	0.17 "	Fe^2O^3	0.18 "
SiO^2	3.14 "	CO^2	42.42 "

Required.—The weight of limestone to be used to make: (1) A slag containing 33.74 per cent, of silica. (2) A slag in which the ratio of silica to bases is 0.516. (3) A slag in which the ratio silica to summated lime is 0.478.

Solution.—This problem embodies the conditions which con-

front the metallurgist when desiring to calculate the flux needed by any given furnace, and we have assumed certain working ratios to be aimed at in the slag, in order to elucidate the method of solution.

CONSTITUENTS OF SLAG.

	From Ore and Fuel.	*From Flux.*	*Total.*
SiO^2	70.9	$0.0314\,x$	$70.9+0.0314\,x$
Al^2O^3	11.6	$0.0032\,x$	$11.6+0.0032\,x$
CaO	39.9	$0.5374\,x$	$39.9+0.5374\,x$
MgO	15.5	$0.0017\,x$	$15.5+0.0017\,x$
FeO	3.2	$\frac{144}{160}(0.0018\,x)$	$3.2+0.0016\,x$
MnO	9.3	.....	9.3 .....
K^2O	3.4	.....	3.4 .....
CaS	0.4	.....	0.4 .....
	154.2	$0.5753\,x$	$154.2+0.5753.x$

(1) To make a slag with 33.74 per cent. of silica we must have

$$70.9+0.0314\,x = 0.3374\,(154.2+0.5753\,x)$$

whence $x = \underline{116}$ pounds.

(2) To make a slag with ratio of silica to bases 0.516 we must have

$$70.9+0.0314\,x = 0.516\,(82.9+0.5439\,x)$$

whence $x = \underline{116}$ pounds.

(3) To make a slag with ratio of silica to summated lime 0.478, we must first summate the lime as follows:

Lime $= 39.9+0.5374\,x$

Lime equiv. of $Al^2O^3 = \frac{168}{102}(11.6+0.0032\,x) = 19.1+0.0053\,x$

" " MgO $= \frac{56}{40}(15.5+0.0017\,x) = 21.7+0.0024\,x$

" " FeO $= \frac{56}{72}(3.2+0.0016\,x) = 2.5+0.0012\,x$

" " $MnO = \frac{56}{71}(9.3) = 7.3$

" " $K^2O = \frac{56}{94}(3.4) = 2.0$

Summated lime $= 92.5 + 0.5463\,x$

therefore

$$70.9 + 0.0314\,x = 0.478\,(92.5 + 0.5463\,x)$$

whence $x = \underline{116}$ pounds.

Comparison of Fuels, Fluxes and Ores.

By properly utilizing the preceding principles, it is possible to compare different varieties of fuels, fluxes or ores with each other, and thus to determine their relative values to the furnace, as far as can be inferred from their chemical composition. (Some of the following methods are from a paper by Mr. F. W. Gordon, Trans. Am. Institute Mining Eng., 1892, p. 61.)

Comparison of Fuels.

If different qualities of fuel are available it is possible to calculate which is the most advantageous to use in the furnace. The fixed carbon only is efficient for the furnace, and not all of that, because the ash of the fuel needs to be fluxed to slag. and a certain amount of the fixed carbon will need to be burned simply to melt this slag. Then the cost of the limestone to be used to flux this ash must be counted in, and finally part of the labor costs of running the furnace must be charged against the slag. We can thus calculate the total charges against the fuel to supply one part of available carbon, which is the best basis upon which to compare different fuels.

Illustration.—Two varieties of coke are available for a blast furnace, analyzing respectively:

	No. 1.	No. 2.
Fixed carbon	84 per cent.	90 per cent.
Volatile matter	2 "	1 "
Moisture	5 "	3 "
Ash	9 "	6 "

And costing respectively $4.50 and $5.50 per ton. The ash of the fuels analyzes respectively:

	No. 1.	No. 2.
Silica	55 per cent.	25 per cent.
Alumina	25 "	5 "
Lime	15 "	50 "
Magnesia	5 "	10 "
Ferric oxide	— "	10 "

They are to be fluxed with the limestone of preceding problem, assumed to cost $1.00 per ton, and to make a slag carrying 40 per cent. of silica and alumina together. Assume an average of 0.228 parts of fixed carbon necessary to melt down 1 part of slag, and that the manufacturing costs borne by the slag amount to $1.00 per ton. What are the relative values of the two fuels in this furnace?

Solution.—The amounts of flux needed to 100 parts of each fuel burned will be found as follows, letting x be the amount of flux used:

	Slag No. 1.	Slag No. 2.
Silica	$4.95+0.0314\,x$	$1.50+0.0314\,x$
Alumina	$2.25+0.0032\,x$	$0.30+0.0032\,x$
Lime	$1.35+0.5374\,x$	$3.00+0.5374\,x$
Magnesia	$0.45+0.0017\,x$	$0.60+0.0017\,x$
Ferrous oxide	$0.0016\,x$	$0.54+0.0016\,x$
Total weights	$9.00+0.5753\,x$	$5.94+0.5753\,x$

Therefore, in case No. 1:

$$7.20+0.0346\,x = 0.40\,(9.00+0.5753\,x)$$

whence $x = 18.4$

And in case No. 2:

$$1.80+0.0346\,x = 0.40\,(5.94+0.5753\,x)$$

whence $x = -2.9$

The negative value in case No. 2 simply means that the ash of fuel No. 2 is more basic than the slag, and, therefore, requires no limestone, but itself acts as a basic flux. Per ton of fuel burned, there would be required respectively 0.184 and -0.029 tons of limestone, and the weights of slag would be 0.196 tons and 0.0427 tons. (Substituting values of x in the total weights of slags.)

The weights of fixed carbon necessary to smelt these weights of slag would be:

No. 1. $0.196 \times 0.228 = 0.0447$ tons.
No. 2. $0.0427 \times 0.228 = 0.0097$ "

Leaving as available fixed carbon for the furnace in each case:

No. 1. $0.84 - 0.0447 = 0.7953$ tons.
No. 2. $0.90 - 0.0097 = 0.8903$ "

From these figures the cost of 1 ton of available carbon furnished by each fuel, adding in manufacturing cost chargeable against the slag, is

No. 1.

Cost of coke, $\$4.50 \div 0.7953$	$= \$5.658$
Cost of limestone, $\$1.00 \times 0.184 \div 0.7953$	$= 0.231$
Costs against slag, $\$1.00 \times 0.196 \div 0.7953$	$= 0.246$
	$\$6.135$

No. 2.

Cost of coke, $\$5.50 \div 0.8985$	$= \$6.233$
Cost of limestone, $\$1.00 \times (-0.092) \div 0.8903$	$= -0.101$
Cost against slag, $\$1.00 \times 0.0065 \times 0.8903$	$= 0.007$
	$\$6.139$

The two fuels, at the prices given, are therefore of almost exactly the same value to the furnace.

The solution along the lines shown is general, for any desired composition of slag, or for use with any given limestone, and is a valuable means of comparing the values of different fuels. The cost of a ton of pure, available carbon, when furnished by any given fuel, is an item which is useful when comparing the relative values of different fluxes or ores with each other.

Comparison of Fluxes.

If different qualities of flux are available it is very desirable to be able to calculate which is the most economical to use in the furnace. Any acid ingredients in the flux diminish very sharply its efficient fluxing power, because they must first be satisfied from the bases present in the same proportions as acid to bases in the final slag. The slag thus formed from the impurities requires further to be melted, and other costs are properly chargeable against it. The best comparison is finally

obtained by calculating for each flux available the cost from it of pure net lime, or net summated lime, analogous to the calculation for pure net carbon in the case of fuels. Any ordinary condition may be imposed upon the slag which the furnace is to produce.

Illustration.—There are available for a furnace two qualities of limestone, containing respectively:

CaO	53.74 per cent.	47.80 per cent.
MgO	0.17 "	4.61 "
SiO^2	3.14 "	5.12 "
Al^2O^3	0.32 "	3.36 "
Fe^2O^3	0.18 "	1.10 "
CO^2	42.42 "	37.55 "

The first costs \$1.00 per ton, the second \$0.80. Assume them smelted with fuel furnishing pure available fixed carbon at \$6.135 per ton; that 0.228 tons of pure fixed carbon is needed to smelt 1 ton of slag; that manufacturing costs against slag are \$1.00 per ton, and that the slag to be made in the furnace must have summated silica equal to summated lime. Compare the relative values of the two fluxes.

Solution.—We will direct our calculations towards finding the net cost of 1 ton of pure available summated lime from each of the two limestones. The summated lime and silica in each flux are:

	No. 1.	No. 2.
Summated lime	0.5411	0.5502
Summated silica	0.0342	0.0808
Excess of summated lime	0.5069	0.4694

The weights of slag formed from the impurities present in each limestone will be:

	No. 1.	No. 2.
CaO (difference between amount present and excess of summated lime found)	0.0305	0.0086
MgO	0.0017	0.0461
FeO	0.0016	0.0099
SiO^2	0.0314	0.0512
Al^2O^3	0.0032	0.0336
Totals	0.0684	0.1494

The cost of 1 ton of pure available lime from each of these fluxes will therefore be, adding in costs chargeable against the slags formed by the impurities present:

No. 1.

Cost of limestone, $\$1.00 \div 0.5069$	$= \$1.973$
Cost of carbon for melting slag, $\$6.135 \times 0.228 \times 0.0684 \div 0.5069$	$= 0.188$
Costs of running, chargeable against slag, $\$1.00 \times 0.0684 \div 0.5069$	$= 0.135$
	$\$2.296$

No. 2.

Cost of limestone, $\$0.80 \div 0.4694$	$= 1.904$
Cost of carbon for melting slag, $\$6.135 \times 0.228 \times 0.1494 \div 0.4694$	$= 0.465$
Cost of running, chargeable against slag, $\$1.00 \times 0.1494 \div 0.4694$	$= 0.318$
	$\$2.487$

The conclusion is that the poorer limestone, at \$0.20 per ton less cost, is in reality costing \$0.191 per ton more for pure available lime, or is in reality 8.3 per cent. dearer than the first, instead of being 20 per cent. cheaper.

The method of calculation here described is quite general for any compositions of limestone or other flux, and for any assumed conditions which the slag must conform to.

Comparison of Ores.

As the more complicated, we come to the comparison of various ores which may be at the iron master's disposal. Here a similar method of procedure is advisable. It can be calculated first, for a unit weight of ore, how much pure lime would be required to flux its impurities, how much pure carbon would be required to melt the slag thus formed, and to the costs of each of these would be added the handling of the slag. Each of these can be also expressed per unit of pure oxide of iron in the ore; and if to their sum we add the cost of ore necessary to furnish unit weight of pure oxide of iron we obtain the total costs per unit weight of pure iron oxide (Fe^2O^3). This is the basis on which different ores may then be compared. It must not be forgotten that one ore may, because of higher sulphur

content, require the production of a more basic slag, so that the amounts of flux required and slag formed will be influenced by the condition necessary to impose on the slag in each case.

Illustration.—The iron ore briquettes (of Problem 51) contained Fe^2O^3, 85.93 per cent.; FeO, 3.96; SiO^2, 5.50; MnO, 0.63; Al^2O^3, 0.76; CaO, 2.23; MgO, 0.97 per cent. If these cost $4.40 per ton, and are smelted in a furnace making slag with ratio of silica to bases 0.516, and assuming 0.3 per cent. of the iron, 82.7 per cent. of the silica, and 96.6 per cent. of the manganese to go into the slag, what is the cost per ton of pure Fe^2O^3 from this source, charging pure lime for fluxing at $2.296 per ton, pure carbon for smelting slag at $6.135 per ton, and requiring 0.228 tons of carbon for one of slag, adding also manufacturing costs at $1.00 per ton of slag?

Solution.—The slag-forming ingredients from 1 ton of ore briquettes are:

$$\text{FeO } 0.003 \times \frac{72}{56} \times \left[\left(0.8593 \times \frac{112}{160}\right) + \left(0.0396 \times \frac{56}{72}\right)\right] = 0.0024 \text{ tons}$$

MnO 0.966×0.0063	= 0.0061	"
CaO	= 0.0223	"
MgO	= 0.0097	"
Al^2O^3	= 0.0076	"
SiO^2	= 0.0455	"
and the bases to satisfy the silica present must be $0.0455 \div 0.516$	= 0.0882	"
But, sum of bases already present	= 0.0482	"
therefore, pure lime to be added	= 0.0417	"
and total weight of slag	= 0.1337	"
Efficient Fe^2O^3 in 1 ton of ore	= 0.8593	"
plus Fe^2O^3 equivalent of reduced FeO $= \frac{160}{144}(0.0396 - 0.0024)$	= 0.0413	"
Total available Fe^2O^3	= 0.9006	"

Cost of 1 ton pure available Fe^2O^3 from these briquettes:

Cost of ore, $\$4.40 \div 0.9006$	$= \$4.885$
Cost of pure lime, $\$2.296 \times 0.0417 \div 0.9025$	$= 0.106$
Cost of carbon for melting slag, $\$6.135 \times 0.228 \times 0.1337 \div 0.9025$	$= 0.207$
Costs chargeable against slag, $\$1.00 \times 0.1337 \div 0.9025$	$= 0.148$
Total	$= \$5.346$

A similar calculation is possible with any ore of any given composition, and making any assumed quality of slag. The costs of 1 ton of pure ferric oxide thus calculated will give the relative costs of the iron obtained from these different sources, and therefore indicate the relative values of the different ores to the blast furnace manager.

Problem 53.

Assume a blast furnace manager to use the ore of preceding illustration, furnishing pure Fe^2O^3 at a net cost of \$5.336 per ton, and to use with it fuel furnishing pure carbon at \$6.135 per ton, there being required for reduction and melting the iron produced and furnishing it with carbon, 0.66 tons of pure available carbon per ton of pig iron produced, and the pig iron containing 96.656 per cent. of iron. The running costs of the furnace are \$3.00 per ton of pig iron produced (costs against slag not included).

Required:—The cost of the pig iron per ton.

Solution:

Fe^2O^3 required $160 \div 112 \times 0.96656$	$= 1.3808$ tons.
Cost of the ore, $\$5.336 \times 1.3808$	$= \$7.368$
Cost of fuel, $\$6.135 \times 0.66$	$= 4.049$
Cost of manufacturing (share against pig iron)	$= 2.000$
Total cost	$= \$13.417$

CHAPTER III.

UTILIZATION OF FUEL IN THE BLAST FURNACE.

The blast furnace, in its simplest terms, may be regarded as a huge gas producer, producing in the region of the tuyeres pure producer gas from fixed carbon and heated air; the gas thus produced is partly oxidized in its ascent through the furnace by the oxygen abstracted from the charge (which latter item is almost a constant quantity per unit of pig iron made), and has added to it carbon dioxide from the carbonates of the charge. But, after all, the unoxidized and combustible ingredients of the gas escaping represent a large part, in fact, often the largest part, of the total calorific power of the fuel.

Problem 54.

A blast furnace uses 2,240 pounds of coke, containing 90 per cent. fixed carbon and 350 pounds of limestone, containing 10 per cent. of carbon (as carbonic acid, CO^2) to produce a ton of pig iron containing 4 per cent. of carbon. The gases contain 24 per cent. of carbonous oxide, CO, 12 per cent. of carbonic oxide, CO^2, 2 per cent. of hydrogen, 2 per cent. of methane, and 60 per cent. of nitrogen.

Required.—(1) The volume of gas, as analyzed, produced per ton of pig iron made.

(2) The calorific power of the gas.

(3) The proportion of the calorific power of the coke which has been generated in the furnace.

Solution.—(1) The carbon going into the gases will be that in the coke, less that in the pig iron, plus that in the carbonates of the charge.

Carbon in coke	$= 2{,}240 \times 0.90 =$	2,016	pounds
Carbon in carbonates	$= 350 \times 0.10 =$	35	"
Carbon charged	$=$	2,051	"
Carbon in pig iron	$= 2{,}240 \times 0.04 =$	89.6	"
Carbon going into the gases	$=$	1,961.4	"

Carbon in 1 cubic foot of gas:

In CO 0.24×0.54
In CO^2 0.12×0.54
In CH^4 0.02×0.54

Total $0.38 \times 0.54 = 0.2052$ ounces av.
$= 0.012825$ pounds

Gas produced per ton of pig iron $= \frac{1,961.4}{0.012825} = 152,935$ cu. ft. (1)

(2) Calorific power of 1 cubic foot of gas:

CO $0.24 \times 3,062 = 734.9$ oz. cal.
H^2 $0.02 \times 2,613 = 52.3$ "
CH^4 $0.02 \times 8,598 = 172.0$ "

Sum $= 959.2$ "
$= 59.95$ pound cal.
per 152,935 cubic feet $= 9,168,450$ pound cal. (2)

(3) The calorific power of the coke considering it to contain simply 90 per cent. of fixed carbon, would be

$8,100 \times 0.90 = 7,290$ pound cal. per pound.

The presence of CH^4 in the gases points, however, to there being probably some available hydrogen in it, which would increase its calorific power somewhat. A closer approximation to the calorific power of the coke could, therefore, be obtained by assuming at least as much available hydrogen in it as would correspond to the hydrogen in the CH^4 in the gas.

CH^4 in 152,935 cu. ft. of gas	=	3,059 cu. ft.
Weight of this $= 3,059 \times (0.09 \times 8)$	=	2,202 oz. av.
	=	137.7 lbs.
Hydrogen $= 137.7 \times (4 \div 16)$	=	34.4 lbs.
Available hydrogen in coke $= 34.4 \div 2,240$	=	1.54 per cent.
Calorific power $0.0154 \times 29,030$	=	447 lb. cal. per lb.
Total calorific power of the coke	=	7,737 " "
Calorific power of coke used per ton $7,737 \times 2,240$	=	17,330,880 lb. cal.
Calorific power of the gases	=	9,168,450 "
Calorific power generated	=	8,162,430 "
	=	47.1 per cent.

This figure, however, practically over-charges the furnace little bit, because the pig iron with its 4 per cent. of carbon really takes out of the furnace some unburnt fuel, whose heat of combustion may be utilized outside the furnace as in the Bessemer converter. The furnace does not generate heat from this, representing:

$$2{,}240 \times 0.04 \times 8{,}100 = 725{,}760 \text{ lb. cal.}$$

leaving as actually generated in the furnace

$$8{,}162{,}430 - 725{,}760 = 7{,}436{,}670 \text{ lb. cal.}$$
$$= 42.9 \text{ per cent.} \qquad (3)$$

Such an average blast furnace cannot, therefore, be accused of generating within it over some 43 per cent. of the calorific power of the fuel put into it, while the heat rejected as potential energy of combustion of the waste gases amounts to more than half the calorific power of the fuel. Fifty years or more ago, when these waste gases were allowed to burn truly to waste the blast furnace was indeed a devourer of fuel, but matters have been improved by the utilization of the waste gases to heat the blast, and thus one of the largest "leaks" of heat from the furnace has been patched up to some extent, although yet far from satisfactorily.

Problem 55.

Assume that in problem 54, one-third of the gases produced are burnt in hot-blast stoves, preheating the air blown in at the tuyeres, and that the blast is thus preheated to 450° C.

Required.—(1) The amount of blast blown in per ton of pig iron made.

(2) The heat in the blast.

(3) The efficiency of the hot-blast stoves.

(4) The increased efficiency of the blast furnace plant as a whole in generating the calorific power of the fuel, when thus provided with this hot-blast apparatus.

Solution.

(1) Volume of (dry) gases per ton = 152,935 cu. ft.
Nitrogen present in these (60%) = 91,761 "

$$\text{Air containing this} = \frac{91{,}761}{0.792} = 115{,}860 \text{ "} \qquad (1)$$

This is the volume of the blast per ton of pig iron produced, assuming no nitrogen to come from the coke used, and the blast to be dry. If the blast were moist, and its hydrometric condition known, the volume of moist blast could be calculated.

(2) Assuming the blast dry, it is heated to 450° C.,requiring

$$115{,}860 \times [0.303 + 0.000027\ (450)] \times 450 = 16{,}430{,}975 \text{ oz. cal.}$$
$$= 1{,}026{,}936 \text{ lb. cal.}$$

(3) The hot-blast stoves receive one-third of all the gas produced, having, therefore, a calorific power of

$$9{,}168{,}450 \div 3 = 3{,}056{,}150 \text{ lb. cal.}$$

$$\text{Efficiency of the stoves} = \frac{1{,}026{,}936}{3{,}056{,}150} = 0.336 = 33.6 \text{ per cent.} \quad (3)$$

(4) The blast furnace was primarily rejecting unused 57.1 per cent. of the calorific power of the fuel, 4.2 per cent., however, as a necessary loss, to supply the carbon in the pig iron, but 52.9 per cent. as combustible power of unburnt waste gases. If one-third of these gases are completely burnt in hot-blast stoves, then the combined plant—furnace plus stoves—is utilizing 17.6 per cent. more of the calorific power of the fuel than before, or $42.9 + 17.6 = 60.5$ per cent., and, therefore, rejecting undeveloped 39.5 per cent. of the calorific power. (4)

[The net effect of the use of the hot-blast stove, upon the heat generation in the furnace, is practically to put back into the furnace, as sensible heat, $1\text{-}3 \times 33.6 = 11.2$ per cent. of the calorific power of the waste gases, equal, therefore, to $0.112 \times 52.9 = 5.9$ per cent. of the total calorific power of the fuel. This renders available, for the working of the furnace, $42.9 + 5.9 = 48.8$ per cent. of the calorific power of the fuel, an increase of available heat for reducing and smelting of $\frac{5.9}{42.9} =$ 13.7 per cent. of the former available quantity.]

The practical conclusion is that a blast furnace generates in itself not much over 40 per cent. of the calorific power of the fuel used, and rejects nearly 60 per cent.; by using part of the waste gases to heat the blast, however, some of this rejected heat, to an amount representing net 5 to 10 per cent. of the calorific power of the fuel used, is returned to and injected

bodily into the furnace, thus rendering available for the purposes of running the furnace some 50 per cent. of the calorific power of the fuel as a maximum. The efficiency with which the furnace applies this 50 per cent. usefully to the objects of reducing and smelting, is another question for investigation.

Problem 56.

Assume that at the furnace of Problems 54 and 55 the two-thirds of the waste gases are burnt under boilers, raising steam which runs the blowing engines, hoists and pumps, and providing 10 effective horse-power for each ton of pig iron made per day in the furnace.

Required.—(1) The efficiency of development of the calorific power of the fuel in the plant (furnace, stoves, boilers, engines) regarded as a whole.

(2) The thermo-mechanical efficiency of the boiler and engine plant.

(3) The power which could be generated if gas engines, at 25 per cent. thermo-mechanical efficiency, were used in their stead.

Solution.—(1) Since the stoves completely burn one-third of the waste gases, and the boilers the other two-thirds, all the combustible power of the waste gases is developed in the combined plant, and the only part of the calorific power of the fuel which is unused is the 4.9 per cent, represented by the carbon necessarily entering into the composition of the pig iron. The plant as a whole, therefore, develops or generates 95.1 per cent. of the calorific power of the fuel used.

(2) For each ton of pig iron, the heat developed under the boilers will be two-thirds of the calorific power of the gases, or

$$9{,}168{,}450 \times 2\text{-}3 = 6{,}112{,}300 \text{ lb. cal.}$$

There is generated thereby 10 effective horse-power days, equal to

$$10 \times 33{,}000 \times 60 \times 24 = 475{,}200{,}000 \text{ ft. lbs}$$

$$\text{But 1 lb. cal.} = 425 \times 3.2808 = 1394.3 \text{ "}$$

Therefore, thermal equivalent of

$$\text{work done} = \frac{475{,}200{,}000}{1394.3} = 340{,}800 \text{ lb. cal.}$$

Thermo-mechanical efficiency of boiler and engine plant:

$$\frac{340{,}800}{6{,}112{,}300} = 0.0557 = 5.57 \text{ per cent.} \qquad (2)$$

(3) Gas engines, at 25 per cent. thermo-mechanical efficiency, would give power representing per ton of pig iron produced:

$$6{,}112{,}300 \times 0.25 = 1{,}528{,}075 \text{ lb. cal.}$$

Equal to $1{,}528{,}075 \times 1394.3 = 2{,}130{,}645{,}900$ ft. lbs.

or $$\frac{2{,}130{,}645{,}900}{33{,}000 \times 60 \times 24} = 44.9 \text{ horse-power days.} \qquad (3)$$

A quicker solution is:

$$10 \times \frac{25}{5.57} = 44.9 \quad \text{“} \quad \text{“} \qquad (3)$$

Leaving net *surplus* power per ton of pig iron produced per day = 34.9 horse-power.

The preceding problems have elucidated the question of the small proportion of the calorific power of the fuel which is generated in a blast furnace, showing it to be, in usual practice only 40 to, at most, 50 per cent. of the calorific power. The discussion has not explained “ why,” but a further consideration will throw light on this question also.

The proportion of the calorific power of a fuel which is generated in a blast furnace is solely a question of how much of it is burned to carbonic oxide, CO^2, and how much to carbonous oxide, CO? If all the carbon were burned to CO^2, practically all the calorific power of the fuel would be generated; if all were burned to CO, only $\frac{2{,}430}{8{,}100} = 0.30 = 30$ per cent. of the heating power of the carbon would be generated. If a blast furnace was filled with nothing but coke, and air blown in as usual at the tuyeres, carbon would be burned in the furnace only to CO, and but 30 per cent, of its calorific power be generated and available for the needs of the furnace. The entire gain over this percentage is due to the oxidation of CO to CO^2 by the oxygen abstracted from the solid charges, that is, by the act of reduction. In Problem 54 we calculated that under ordinary conditions, between 40 and 50 per cent. of the calorific

power of the fuel is generated in the furnace; the excess of this above 30 per cent. is due to the oxidation of CO to CO^2 during the reduction of the metallic oxides in the charge. From this standpoint it is advisable to strive to perform the greatest possible proportion of the reduction in the furnace by CO gas, because in this case the total generation of heat in the furnace per unit of fuel charged will tend towards a maximum. Since no carbon can be burned to CO^2 at the tuyeres, it follows that, *from the standpoint of the generation of the maximum quantity of heat in the furnace, from a given weight of fuel*, Grüner was right in formulating his dictum of the ideal working of a blast furnace, viz.:

GRÜNER'S "IDEAL WORKING."

All the carbon burnt in the furnace should be first oxidized at the tuyeres to CO, and all reduction of oxides above the tuyeres should be caused by CO, which thus becomes CO^2. This dictum is not in Grüner's own words, but expresses their sense, and from the point of view of the present discussion, it is the correct principle upon which to obtain the maximum generation of heat in the furnace from a given weight of fuel. It practically directs us to generate at the tuyeres 30 per cent. of the calorific power of the carbon oxidized in the furnace, and the rest that can be obtained from the carbon is to be generated during the reduction of the charge.

If we apply this principle to the furnace and data of Problem 54, we should first observe that the carbon oxidized in the furnace is:

Carbon in coke charged	2016.	pounds
Carbon in pig iron produced	89.6	"
Carbon oxidized in furnace	1926.6	"

Requiring, if all oxidized to CO at the tuyeres

$$1926.6 \times \frac{4}{3} \text{ lbs. oxygen} = 2569. \text{ pounds.}$$

But, Problem 52 shows us that there was actually blown into this furnace 115,860 cubic feet of blast, containing, therefore,

$$115{,}860 \times 0.208 \times (1.44 \div 16) = 2{,}169 \text{ lbs. oxygen,}$$

capable of oxidizing to CO at the tuyeres

$$2{,}169 \times 0.75 = 1{,}627 \text{ lbs. carbon.}$$

Proportion of carbon gasified burnt at the tuyeres,

$$\frac{1{,}627}{1926.6} = 0.844 = 84.4 \text{ per cent.}$$

It is, therefore, true of the furnace under discussion, that if Grüner's ideal working be called standard, this furnace attains to 84.4 per cent. of that ideal; and it is also true that this furnace generates from the carbon burnt at the tuyeres 84.4 per cent. of the amount of heat which could have been generated if Grüner's ideal working had been attained.

It is always possible to find out for any given blast furnace, by similar calculations, how much carbon is burned at the tuyeres, and how much is burned above the tuyeres, and thus to determine how closely the furnace running approximates to Grüner's ideal working. This proportion or percentage will not necessarily express how efficiently the furnace is running, as regards fuel used per unit of iron made, but it will tell what proportion of the calorific power of the fuel used is being generated at the tuyeres, and in possibly nine cases out of ten this proportion indicates the general efficiency of the furnace as regards fuel consumption.

It will be next profitable to inquire when and under what conditions Grüner's ideal working does not correspond to maximum fuel economy, and why it usually does. The answer is not difficult to understand: if all the carbon gasified in the furnace is burned to CO at the tuyeres, 30 percent of the total calorific power of the carbon burned is there developed, which is more than half of all the heat generated from carbon in the furnace. To this must also be added the sensible heat in hot blast, which may amount (as in Problem 52) to some 5.9 per cent. of the calorific power of the carbon, making, therefore, a total of 35 per cent. of the calorific energy of the fuel generated at the tuyeres out of a total of about 50 per cent. developed in the furnace. If, however, the blast be heated to a very high temperature, or particularly if it be dried, or if the ore and fuel are extra pure, so that a smaller quantity of heat is needed to melt down slag at the tuyeres, then there may not

be needed at the tuyeres the generation by combustion of so much heat as Grüner's ideal working would require and cause to be produced, and to burn at the tuyeres all the carbon oxidized in the furnace would be wasteful of fuel. In this case although less heat would be generated per unit of fuel, by burning some of it above the tuyeres, yet economy in fuel consumption as a whole would be attained, because of the *better distribution* of the heat which was generated from a smaller total quantity of fuel.

Illustration.—In Problem 55 we assumed that the furnace ran with blast heated to 450° C., and that this hot blast, burning at the tuyeres 84.4 per cent. of all the carbon gasified in the furnace, smelted down pig iron and slag satisfactorily and kept the tuyere region at proper temperature. If the temperature of this blast were raised to 900° C., how much greater proportion of heat would be available in the tuyere region?

We have already calculated that the 115,860 cubic feet of blast used per ton of iron made, brought in at 450° C., 1,026,936 pound calories of heat, equal to 5.9 per cent. of the calorific power of the fuel put into the furnace. If the temperature were 900° C., the heat brought in would be

$$115{,}860 \times [0.303 + 0.000027\,(900)] \times 900 = 37{,}920{,}978 \text{ oz. cal.}$$
$$= 2{,}370{,}061 \text{ lb. cal.}$$

which equals

$$\frac{2{,}370{,}061}{17{,}330{,}880} = 0.137 = 13.7 \text{ per cent.}$$

of the calorific power of the fuel, a gain of 7.8 per cent. added to the heat available in the tuyere region. This causes a very great increase in the smelting-down power of the furnace, enabling the same work per ton of ore smelted to be done with much less consumption of fuel in the tuyere region. An idea of this increased smelting-power may be obtained from the following comparison of heat available for smelting purposes in the tuyere region in the two cases just discussed:

CASE 1.

Heat developed by oxidation of carbon per ton of iron made, 1,627 lbs. × 2,430	= 3,953,610 lb. cal.
Sensible heat in blast at 450° C.	= 1,026,936 "
Total heat available	= 4,980,546 "

CASE 2.

Heat developed by same quantity of air burning same carbon	= 3,953,610	"
Sensible heat in blast at 900° C.	= 2,370,061	"
Total heat available	= 6,323,671	"

It is, therefore, seen that the heat generated and available at the tuyeres is increased 1,343,125 calories, amounting to 27 per cent. of the amount disposable in Case 1. It follows, therefore, that the smelting down power has been increased 27 per cent., and that, if the 4,980,546 calories were sufficient for satisfactorily smelting down the iron and slag in the first instance, that the extra heat of Case 2 can all be utilized for smelting down 27 per cent. extra burden. We can, therefore, charge 27 per cent. more burden per unit weight of coke in Case 2, because we have the requisite smelting down power at the region of the tuyeres, which amounts to saying that we can charge 22 per cent. less coke for a given weight of pig iron made.

In actual practice, as the amount of burden is increased and the temperature of the blast increased, the change causes more and more of the carbon to be oxidized above the tuyeres, and a smaller proportion to be oxidized at the tuyeres, thus obtaining less service in the furnace from oxidation of carbon as a whole, but compensating for this by the extra heat in the hot blast. Or, looking at it in another way, we may say that the same heat could be made available in the region of the tuyeres, when using hot blast, by the combustion there of a smaller quantity of carbon; therefore, we can burn more of it above the tuyeres and yet work more economically on the whole, than we were working in the first instance, with the colder blast.

MINIMUM CARBON NECESSARY IN THE FURNACE.

Many writers have assumed that in the reduction of iron, oxide, such as Fe^2O^3, the reaction of its reduction by carbonous oxide, CO, is expressed as follows:

$$Fe^2O^3 + 3CO = 2Fe + 3CO^2$$

If this were true, there would need to be burnt to CO at the

tuyeres only 3C, or 36 parts of carbon, to ensure the reduction of Fe^2O^3, representing 112 parts of iron. The reaction does not, however, progress as shown, because CO^2 acts oxidizingly on Fe to such a degree that when $1CO^2$ is present in the gas for 1CO left unused, the reduction practically stops, even though the gases are moving slowly through the warm ore. The real reaction of reduction by CO gas is therefore more nearly represented by

$$Fe^2O^3 + 6CO = 2Fe + 3CO + 3CO^2,$$

which shows that 112 parts of iron would require at least 72 parts of carbon to be oxidized at the tuyeres to CO, in order to produce the gas necessary for its reduction. The presence of some CO^2 in the furnace coming directly from carbonates in the charge would neutralize still more of the reducing power of the CO gas, and cause still more of it to be theoretically required for reduction. The minimum amount of carbon necessary to be charged in the furnace will be that necessary to furnish fixed carbon enough for this reducing gas and for the carbon in the pig iron. This would be, per 100 parts of pig iron, containing say 93 iron and 3 carbon, and using coke containing 90 per cent. of fixed carbon:

Carbon burnt at tuyeres $= 72 \times 93 \div 112$	$= 59.8$
Carbon in pig iron	$= 3.0$
Total fixed carbon necessary	$= 62.8$
Total coke to supply this $= 62.8 \div 0.9$	$= 69.8$

It results from these calculations that if "Grüner's ideal working" of a blast furnace were carried out to the practical extent of reducing all the charge by carbonous oxide, CO, and oxidizing no carbon at all directly above the tuyeres, that about 63 parts of fixed carbon would be required per 100 of pig iron made, requiring from 70 to 80 parts of fuel, according to its richness in fixed carbon (90 to 80 per cent.). In practice, as is well known, *more* than this is commonly used, because of the larger proportion of unused CO in the gases than above assumed: and *less* than this has been regularly used, showing that economy of fuel can be attained without adhering to "Grüner's ideal working," in fact, by transgressing it as far as one dares.

The principle involved can be best grasped by a calculation of the amount of carbon which would be required by the furnace, supposing all the heat necessary for melting down the charge were supplied by electrical means, thus dispensing, for the purposes of this supposition, with the necessity of blast and the consequent necessity of oxidizing any carbon by any other agent than the oxygen given up by the ore. In this case the gases resulting would be, let us assume, of the same composition as before, that is, containing equal volumes of CO and CO^2, and since this oxygen is abstracted altogether from the ore, the reaction is

$$Fe^2O^3 + 2C = 2Fe + CO + CO^2$$

This would represent the utilization of carbon in an electrically-heated furnace, and would require per 100 of pig iron made, assuming it 3 per cent. carbon and 93 iron:

Carbon for reduction $24 \times 93 \div 112$	$= 19.9$
Carbon in pig iron	$= 3.0$
Total fixed carbon necessary	$= 22.9$

Or only a little over one-third as much as the minimum required when the smelting down is done by blast.

Aside from electrical furnace practice, however, this discussion proves that whatever fixed carbon burns or oxidizes above the region of the tuyeres, in a blast furnace, absorbs oxygen from the charges with three times the efficiency of carbon first burnt at the tuyeres. Every pound of oxygen abstracted from the charges by solid carbon requires the use or intervention of only one-third as much carbon as that which is abstracted by CO gas; or, each pound of carbon abstracting oxygen directly from the charge takes from it three times as much oxygen as a pound of carbon first burnt to CO at the tuyeres possibly can.

The ordinary furnace produces at the tuyeres, in order to get heat enough to melt down the charges, *more* CO gas than is needed to abstract all the oxygen from the charges; under these conditions it is uneconomical to oxidize any carbon at all above the tuyeres. The exceptional furnace, because of pure ores, small amount of slag, pure fuel, high temperature of blast, or dry blast, gets heat enough at the tuyeres to melt

down the charges *without* producing enough CO gas to reduce all the charges; under these conditions more or less reduction is effected by solid carbon, and with the greatest economy in quantity of carbon required in the furnace. These are the conditions under which, having passed the turning point, the greater economy of fuel is attained the farther away one can get from " Grüner's ideal working."

CHAPTER IV.

THE HEAT BALANCE SHEET OF THE BLAST FURNACE.

Twenty-eight years ago, Sir Lothian Bell first constructed a satisfactory heat-balance sheet for a blast furnace. His observations were largely, and his experience altogether, confined to the reduction of the argillaceous siderite ores of the Cleveland district, England, and although he made numerous attempts to draw general conclusions from the data at hand applicable to iron smelting in general, yet many of his deductions remain true only for the particular ores and manner of working characteristic of the Cleveland district.

No treatment of this subject, however, can be based otherwise than upon Bell's researches, following the lines laid down, in his " Principles of the Manufacture of Iron and Steel."

Heat Received and Developed.

The items on this side of the balance sheet are:

(1) Combustion of carbon to carbonous oxide (CO).

(2) Combustion of carbon to carbonic oxide (CO^2).

(3) Sensible heat of the hot blast.

(4) Heat of formation of the pig iron from its constituents.

(5) Heat of formation of slag from its oxide constituents.

(1) and (2) *Combustion of carbon in the furnace.* There is but one satisfactory way to determine with exactness the amounts under this heading. From the balance sheet, the total amount of carbon passing into the gases is obtained; from the analysis of the gases, the weight of carbon per unit volume of gases is calculated; the first divided by the second gives the volume of gases per unit weight of pig iron produced. The amount of CO and CO^2 in these gases is then obtained by use of the gas analysis, and if from the total CO and CO^2 in the gases there be subtracted the CO and CO^2 contributed *as such* by the solid charges, the difference is the CO and CO^2 which have been formed in the furnace. The heat evolved in the formation of these quantities can then be calculated.

Illustration.—In Problem 51 it was calculated that per 1,000 kilos. of pig iron produced, 534.09 kg. of carbon went into the gases; also that the analysis of the gases showed 0.20736 kg. of carbon in each cubic meter of gas. The quotient indicated, therefore, 2575.6 cubic meters of gas produced per ton of pig iron. From the analysis of the gases there was in this volume,

$$2575.6 \times 0.231 = 595.0 \text{ m}^3 \text{ of CO}$$
$$2575.6 \times 0.148 = 381.2 \text{ m}^3 \text{ of CO}^2$$

whose weights were

$$595.0 \times 1.26 = 749.7 \text{ kg. CO}$$
$$381.2 \times 1.98 = 754.8 \text{ kg. CO}^2$$

The balance sheet shows, however, 49.1 kg. of CO^2 contained in the limestone flux used, which can be assumed as entering the gases bodily. Subtracting this we have 705.7 kg. of CO^2 formed in the furnace, and 749.7 kg. of CO, containing respectively

$$705.7 \times \frac{12}{44} = 192.5 \text{ kg. of C in } CO^2$$

$$749.7 \times \frac{12}{28} = 321.3 \text{ kg. of C in CO}$$

The heat generated in the furnace by the oxidation of carbon is, therefore,

$$192.5 \times 8100 = 1{,}559{,}250 \text{ Calories}$$
$$321.3 \times 2430 = \quad 780{,}760 \quad \text{“}$$
$$\overline{\qquad\qquad\qquad}$$
$$2{,}340{,}010 \quad \text{“}$$

If this carbon could have been entirely burnt to CO^2, there would have been generated

$$513.8 \times 8100 = 4{,}161{,}780 \text{ Calories}$$

Showing that only 56 per cent. of the calorific power of the carbon was developed in the furnace; the other 46 per cent. exists as potential calorific power in the waste gases, and part

of it is really put back into the furnace as sensible heat in the hot blast.

There is a little doubt as to how to consider the CH^4 in the gases; that is, whether the heat of its formation should be reckoned in as developed in the furnace. This would be (C,H^4) = 22,250, or 1,854 Calories per kg. of carbon contained therein. Its presence in the gas probably results largely from the distillation of the fuel at a high temperature, and the heat required to disunite the CH^4 from the solid fuel is probably as great as is represented by its heat of formation from carbon and hydrogen. The item is, therefore, a doubtful one, and as far as we know, we may be coming about as near to the truth by omitting it altogether as by counting it in. If we wished to add it in the illustration just given the calculation would be:

Volume of CH^4	= 2575.6 $\times$0.005	= 12.88 m^3
Weight of C	= 12.88$\times$0.54	= 6.9 kg.
Heat of formation	= 6.9 $\times$1,854	= 12,793 cal.

It should be emphasized that in this calculated heat of oxidation of carbon in the furnace, no account has been taken whatever of *where* in the furnace this heat is generated. Above all, the mistake should not be made of supposing that the 780,760 Calories produced by formation of CO represents the heat generation at the region of the tuyeres; nothing could be further from the truth. A great deal of carbon is burnt to CO at the tuyeres, and some above the tuyeres, but a goodly proportion of this CO oxidizes by abstracting oxygen from the charge and becomes CO^2. It would not be incorrect, however, to divide the heat of oxidation of carbon in the furnace into two parts, viz: to assume all the carbon as first forming CO, and part of this CO afterwards forming CO^2, corresponding to the amount of the latter formed in the furnace. If this were done, we would have

513.8 kg. C to CO	= 513.8$\times$2430	= 1,248,535 Cal.
449.2 kg. CO to CO^2	= 449.2$\times$ 2430	= 1,091,475 "
		2,340,010 "

This analysis gives us the information that of the total heat generated by the oxidation of carbon in the furnace, some-

where about one-half is generated by its burning to CO, and the other half by the further oxidation of CO to CO^2; and we also know that the larger part of the former takes place at the tuyeres, and all of the latter takes place during the reduction of the charges in the upper part of the furnace.

If we know, however, or have calculated the amount of the blast received by the furnace, or, more properly speaking, the amount of oxygen in the blast, then the heat generated by oxidation of carbon at the tuyeres becomes known. In the previous illustration, taken from Problem 51, we can also take from the same problem the weight of oxygen in the blast, 557.7 kilos. This would burn $557.7 \times 0.75 = 418.3$ kg. of carbon to CO at the tuyers, generating there

$$418.3 \times 2430 = 1{,}016{,}410 \text{ Calories},$$

or 44 per cent. of all the heat generated by oxidation of carbon in the furnace, leaving 1,323,610 Calories as generated above the tuyeres by the agency of the oxygen of the charges. These figures tell us just where and how the principal items of heat were generated in this particular furnace, and the similar calculation may be made for any blast furnace for which we have the necessary data.

(3) *Sensible heat in the hot blast.* To calculate this item, we need to know the weight or volume of the different constituents of the blast and their temperature. The question at once arises, as to what base line of temperature shall be chosen. It is most convenient to choose 0° C., since that is not over 15° from the average temperature in the largest iron producing countries. However, any other prevailing temperature may be taken as the base line, involving merely a little more calculation, since our specific heats are reckoned from 0° C. The temperature ought, moreover, to be taken as near to the tuyeres as possible, to properly take into account the effect of cooling of the blast in the bustle and feeder pipes, from radiation and expansion. The blast consists of air p oper and moisture, the former with a mean specific heat between 0° and t° C of $0.303 + 0.000027t$, in kilogram Calories per cubic meter, or in ounce calories per cubic foot, the latter with a similar mean specific heat of $0.34 + 0.00015t$. Since the moisture at times amounts to as much as 5 per cent. of the blast, it should be calculated separately.

Illustration: With the outside air at 30° C., and saturated with moisture (raining), calculate the heat carried into a blast furnace by blast carrying in 1859.1 kilos. of nitrogen, the temperature of the heated blast being 600° C. Barometer 720 millimeters of mercury. Temperature base line 0° C.

Solution: One cubic meter of the moist blast, as taken into the blowing cylinders, carries all the moisture it can hold, the tension of which is therefore 31.5 millimeters. The tension of the air proper present is therefore 720—31.5 = 688.5 millimeters, and each cubic meter of moist air carries

$$\frac{31.5}{720} = 0.0438 \text{ cubic meter of moisture, and}$$

$$\frac{688.5}{720} = 0.9562 \text{ cubic meter of air proper.}$$

Whatever the temperature of the blast, the moisture and air proper will be in this same proportion whenever its temperature is over 30° C. If the temperature were 0° C. the moisture would be mostly condensed, but for the purposes of calculating the heat brought in we may assume the moist air to be at 0° C., with its moisture uncondensed. That volume of blast which would be 1 cubic meter at 0° and 760 mm. pressure, would, therefore, bring in, at 600° C., the following quantity of heat:

H^2O	$0.0438\times[0.34 + 0.00015\ (600)]\ \times 600$	=	11.3 Calories
Air	$0.9562\times[0.303 + 0.000027\ (600)]\ \times 600$	=	179.7 "
	Total		191.0 "

Since the nitrogen present in this is

$$0.9562\times 1.293\times\frac{10}{13} = 0.9511 \text{ kg.}$$

the heat brought in per 1859.1 kg. of nitrogen is

$$191.0\times\frac{1859.1}{0.9511} = 373{,}344 \text{ Calories.}$$

An amount equal to over one-third of all the heat generated by combustion of carbon at the tuyeres.

(4) *Heat of formation of pig iron from its constituents.* The

pig iron contains several per cent., some 5 to 10 altogether, of carbon, silicon, manganese, phosphorus, sulphur and other elements. The energy of their combination with the iron is a somewhat indefinite quantity, and in no case can be considerable. Berthelot states the energy of combination of carbon with iron as (Fe^3,C) = 8,460, which would be 705 Calories per kilogram of carbon, and another investigator (Ponthière) states the heat of combination of phosphorus with iron to be zero. In the present state of uncertainty it is hardly allowable to add in any other than the heat of combination of the carbon in the iron, and leave out that of the other elements.

(5) *Heat of formation of the slag from its constituent oxides.* Here we touch upon a quantity of more than insignificant proportions, yet which is not yet quantitatively known with satisfactory accuracy. The main constituents of the slag are SiO^2, Al^2O^3, CaO, MgO and CaS, which are provided by clay, limestone and iron sulphide. If we allow, on the other side of the balance sheet, for the heat necessary to de-hydrate clay, drive carbonic acid off carbonates, and break up iron sulphide and enough CaO to furnish Ca for CaS, we are then entitled, on the other hand, to place in the heat evolution column the heat of combination of aluminum silicate with lime and magnesia, the heat of formation of CaS and its heat of solution in the silicate slag. The heat of formation of CaS is 94,300 Calories, or 2,947 Calories per kilogram of sulphur; its heat of combination with a silicate slag is unknown. The heat of combination of lime with aluminum silicate has been determined only for the proportions 3CaO to $Al^2Si^2O^7$, that is, for 168 parts of CaO uniting with 222 parts of aluminum silicate. This has been determined in Le Chatelier's laboratory as (3CaO, $Al^2Si^2O^7$) = 33,500 Calories which is 200 Calories per unit of CaO combining, or 150 Calories per unit weight of $Al^2O^3 + SiO^2$. The calculation would be made on the basis of the amount of lime (plus lime equivalent of magnesia present), if it were present in a smaller ratio than 168 to 222 of silica and alumina, and on the basis of the silica and alumina, if their ratio to the summated lime were less than 222 to 168. It is probable that in the near future these quantities will be known more accurately.

One item of heat received by the furnace has not been men-

tioned, because of its usual absence, viz.: heat in hot charges. Very rarely roasted ore comes hot to the furnace, in which case its sensible heat must be counted in, else the thermal sheet of the furnace will be that much out of balance.

Heat Absorption and Disbursement.

The items on this side of the balance sheet are:

(1) Sensible heat in waste gases, including water vapor only as vapor.

(2) Sensible heat in outflowing slag.

(3) Sensible heat in outflowing pig iron.

(4) Heat conducted to the ground.

(5) Heat conducted and radiated to the air.

(6) Heat abstracted by cooling water, tuyeres, etc.

(7) Heat for de-hydrating the charges.

(8) Heat for vaporizing water from charges.

(9) Heat absorbed by decomposition of carbonates.

(10) Heat absorbed in reduction of iron oxides.

(11) Heat absorbed in reduction of other metallic oxides.

(12) Heat absorbed by decomposition of moisture of the blast.

(1) *Sensible heat in waste gases.* The amount of these gases is known only from the carbon contained in unit volume, by analysis, and the known weight of carbon entering and leaving the furnace. If there is much fine coke carried over by the blast, allowance must be made for the carbon in it, because this would not be represented in the gas analysis. The analysis of completely dried gas is that usually obtained, because if the gas is measured without drying, an uncertain amount of moisture is condensed, and, therefore, it is usual to dry before measuring and analyzing. The amount of moisture in the gases is either assumed as that driven off from the charges, as shown by the balance sheet, or else is determined directly by drawing the gases through a calcium chloride tube or other dessicating apparatus. Several tests should be made to get a fair average, because much more will be in the gases immediately after charging than immediately before. Dust must be excluded from the drying tube by filtering the gases through dry asbestos. The average temperature of the gases should be known over a considerable period; a thermo-couple

in the down-comer gives this most accurately and more uniformly than if inserted above the stock line in the furnace.

The weight of moisture per unit volume of dry gas is then converted into volume at standard conditions by dividing by 0.81 (1cubic meter = 0.81 kg; 1 cubic foot = 0.81 ounce avoirdup.). The sensible heat of the gases is then calculated, using 0° C. as the base line, and the proper mean specific heats of the gases per unit of volume. The water vapor will here be considered simply as a gas, and its sensible heat above water vapor at 0° only calculated. This leaves the latent heat of vaporization of this water to be considered as a separate item (606.5 Calories), that is, as heat absorbed by reactions in the furnace, thus putting it on exactly the same footing as the CO^2 in the gases which has been expelled from carbonates in the furnace. By so proceeding much uncertainty as to the heat in the water vapor is avoided.

If the amount of flue dust is considerable its quantity should be ascertained, and the heat in it also calculated and added in to the heat in the moist gases. Its specific heat may be approximated as so much carbon, iron oxide and silica, the proportions of each of these present being known.

(2) *Sensible heat in outflowing slag.* The weight of slag produced is seldom taken directly, but can be reckoned up with all needful accuracy from the balance sheet of materials entering and leaving. Its temperature and specific heat, solid and liquid, melting point and latent heat of fusion, are unfortunately almost always unknown factors. The one datum which is needful, however, is the total heat in a unit weight of liquid slag as it flows from the furnace, and this is not a difficult quantity to obtain. A rough calorimeter with a reliable thermometer and containing a carefully weighed quantity of water, may be easily constructed. Some liquid slag is run directly into it, and by observing the rise of temperature and afterwards filtering out, drying and weighing the granulated slag, a satisfactory determination can be arrived at. This is corrected to 0° C. by using an approximate specific heat, say 0.20, for the range of final calorimeter temperature to zero. In this connection it is important to note that the calorimetric determinations of Akerman on blast-furnace slags, give the heat in the *just-melted* slag, whereas slags flowing out of a

furnace are considerably, some 200° to 500° C., above their melting point, and therefore contain some 50 to 150 Calories more heat than that given by Akerman for a slag of similar composition. Since Akerman's values run from 350 to 400 Calories, the actual heat in the outflowing slag may be between 400 and 550 Calories. Akerman himself states that an average of twenty-seven Swedish furnaces gave 530 Calories as the actual heat in unit weight of outflowing slag, and Bell uses 550 in most of his calculations on Cleveland (England) furnaces.

(3) *Heat in outflowing pig iron.* The heat in *just-melted* pig iron is evidently too small a quantity to use in this connection. The heat in the outflowing pig iron at 200° to 500° above its melting point will be 50 to 100 Calories greater. The former quantity is about 245 Calories; the latter will be 300 to 350. Bell takes 330 for Cleveland furnaces; Akerman states 250 to 325 for Swedish furnaces. We may conclude then, to use 300 Calories for a coke furnace running cool, and up to 350 Calories for a very hot furnace.

(4) *Heat conducted to the ground.* This is a very uncertain quantity. It varies with the kind of ground, and is more nearly a constant per day than per unit of pig iron produced. It is, therefore, expressed per unit of iron produced, larger for small furnaces run slowly than for large furnaces run fast. It is less when running rich ores and greater with poor ores, other things being equal. As nearly as can be assumed we would put this item as lying between 60 and 200 Calories per unit of pig iron made. Bell uses 169 on one Cleveland furnace, but it is certainly less than 100 in some charcoal furnaces using pure ores and fuel, and consequently with a small heat requirement.

(5) *Heat conducted and radiated to the air.* This item is likewise more nearly a constant quantity per day for a given furnace, and is therefore less per unit of iron produced the faster the furnace is run. It may vary between 60 and 250 Calories per unit of pig iron, the former in furnaces of low heat requirement per unit of iron produced, the latter in those of high heat requirement. If the amount were calculated it would figure out as a time function, and would require the temperature of the outside shell, that of the air, the velocity of the wind, and the total outside surface, in order to calculate

by the principles of heat radiation and conduction, the amount radiated per day. No one has done this yet for any one furnace, and, in brief, items (4) and (5) of this schedule are usually grouped together and determined simply by difference, their sum aggregating from 100 to 500 Calories per unit of pig iron, averaging 100 to 150 for charcoal furnaces of low heat requirement, 200 to 450 for Cleveland furnaces (Bell), and 300 to 500 for large, modern furnaces with thin walls and great height.

(6) *Heat abstracted by cooling water.* In the old-fashioned heavy masonry, cold blast furnace, this item was zero. With the advent of hot blast, the water needed for cooling the tuyeres entered as a heat abstracting factor. It is greater the harder a furnace is blown, but does not increase proportionately with the output. The heat lost by tuyere-cooling water may be 50 to 100 Calories per unit of pig iron made. That for cooling of bosh plates and the outside of the crucible in modern furnaces, may vary all the way up to 200 Calories. These two items are very large in a modern furnace, but are necessary expenditures of heat energy in order to preserve the lines of the furnace during fast running. For any particular furnace they may be determined with all needful accuracy by measuring the amount of water pumped or used for these purposes and its temperature before and after using.

(7) and (8) *Drying and de-hydrating charges.* Water goes into the furnace as moisture and as combined water of the charges. To convert the moisture, such as is evaporated by a current of moderately warm air, into vapor requires 606.5 Calories per unit of water. This allows merely for its vaporization in the furnace, and not for any sensible heat which it may carry out of the furnace at the temperature of the waste gases. This latter item is properly considered in with the sensible heat of the waste gases. The common practice of saying that it takes 637 Calories to evaporate the moisture of the charges is wrong, because this amount would convert water at 0° to vapor at 100°, and, therefore, would include part of what is properly the sensible heat of the waste gases. On the other hand, it is equally wrong to say that this heat of vaporization should be counted in as sensible heat in the hot gases; it would be just as logical or, rather, equally illogical, to count the latent heat of vaporization of CO^2 as sensible heat in the gases.

To drive off water of hydration from hydrated minerals in the charge requires an additional amount of chemically-absorbed heat. As far as is known, this is small for the water driven off hydrated iron oxides, so small as to be a doubtful quantity and safely left out; but if it comes from clay the large amount of 611 Calories is absorbed in merely separating it from its chemical combination ($2H^2O$, $Al^2Si^2O^7$) = 22,000 Calories, which would require 611 + 607 = 1,218 Calories to put into the state of vapor each unit weight of water entering the furnace chemically combined in clay. (This does not concern the ordinary moisture in moist clay, expelled at 100° C., but only the combined water in the dry clay). Where much clay occurs in the ores this quantity becomes important, and its amount explains some of the difficulties met in working clayey charges, particularly since a large part of this chemically combined water is expelled only at a red heat, and, therefore, cools greatly the hotter zones of the furnace.

(9) *Decomposition of carbonates.* Raw limestone, or dolomite, is the usual flux of the blast furnace, and its carbonic acid is evolved at temperatures between 600° and 800°. Whether some of this is subsequently decomposed by contact with carbon and reduced to CO, is immaterial to the balance sheet, because more than enough CO^2 escapes from the furnace to represent the CO^2 of the flux, and we charge the furnace only with the formation of the CO and CO^2 actually found in the gases, less the CO^2 from fluxes. Bell charges up the heat absorbed also in the assumed reaction $CO^2 + C = 2CO$, but this is an error, because it is doubtful how much of the CO^2 is thus decomposed, and the question, in its last analysis, is one of heat *distribution* in the furnace, and does not concern the totals of heat absorbed or evolved. We can, therefore, omit the item of decomposition of this CO^2 (as likewise, and for analogous reasons, the heat evolved in carbon deposition in the upper part of the furnace $-2CO = C + CO^2$), and need consider only the heat required to expel the CO^2 from carbonates. This is:

(CaO, CO^2)	= 45,150 Calories	= 1,026 Calories	per kg. CO^2
(MgO, CO^2)	= 29,300 "	= 666 "	"
(MnO, CO^2)	= 22,200 "	= 500 "	"
(FeO, CO^2)	= 24,900 "	= 566 "	"
(ZnO, CO^2)	= 15,500 "	= 352 "	"

By using the above figures, in connection with the known composition of ore and fluxes, the heat required to decompose carbonates can be correctly calculated.

(10) *Reduction of iron oxides.* The heats of formation of the various oxides of iron are:

(Fe,O)	= 65,700	Calories	= 1,173	Calories	per kg. iron
(Fe^3,O^4)	= 270,800	"	= 1,671	"	"
(Fe^2,O^3)	= 195,600	"	= 1,746	"	"

And, therefore, just these quanities of heat are required per unit weight of iron reduced from these compounds. If the ore is a carbonate the heat absorbed in driving of CO^2 from $FeCO^3$ can be first allowed for, and then the heat required for reduction of the FeO calculated on the weight of the reduced iron. If some FeO goes into the slag it will be as FeO, and if the ore was Fe^2O^3, or Fe^3O^4, the reduction of unit weight of iron from the state of Fe^2O^3, or Fe^3O^4, to the state of FeO, absorbs respectively 573 or 498 Calories, as may be readily deduced from the heats of formation of the three oxides concerned. If FeS is present its heat of formation is

(Fe, S) = 24,000 Calories = 429 Calories per kg. Fe.

If the iron is charged partly as silicate, such as mill or tap cinder, an additional amount of heat will be required for reduction, equal to that needed to separate the iron oxides from their combination with silica. The heat of formation of the bi-silicate slag only has been determined.

(FeO, SiO^2) = 8,900 Calories = 148 Calories per kg. SiO^2.

And since the cinders concerned contain relatively more iron than this, we can best make allowance for the heat required to set free the silica. It is necessary, therefore, to take the amount of silica in the iron cinder charged, and allow, as necessary for its decomposition into FeO and SiO^2, 148 Calories for each unit weight of SiO^2 contained.

(11) *Reduction of non-ferrous oxides.* Silicon is usually present in pig iron, its reduction from silica requiring:

(Si, O^2) = 180,000 Calories = 6,413 Calories per kg. Si.

There is a little doubt about this (Berthelot's) figure; more

recent determinations, not yet published, point rather to 196,000 and 7,000 Calories respectively.

Manganese is often present in the ores as Mn^2O^3, Mn^3O^4, or MnO^2, and going partly into the slag as MnO. The heat absorbed in reduction to manganese is:

(Mn, O)	= 90,900 Calories	= 1,653	Calories	per kg.Mn
(Mn^3, O^4)	= 328,000 "	= 1,988	"	"
(Mn, O^2)	= 125,300 "	= 2,278	"	"

For the MnO produced and going into the slag, the reduction from Mn^3O^4, or MnO^2, per unit weight of contained manganese, absorbs 335 or 625 Calories respectively.

Sulphur generally comes from the reduction of FeS, requiring 667 Calories per kg. of sulphur; but care must be taken not to allow for this heat twice, since if reckoned once under the head of iron reduction it must not be reckoned on the balance sheet a second time under sulphur. One reduction of FeS liberates both constituents.

Phosphorus may be reduced in large quantity in making basic iron. It probably comes mostly from calcium phosphate, in which case we must reckon on not only the heat of oxidation of phosphoric oxide but also its heat of combination with lime:

(P^2, O^5)	= 365,300 Cal.	= 5,892 Cal.	per kg. of P.
(3CaO, P^2O^5)	= 159,400 "	= 2,410 "	" contained.

Making a total heat requirement of 8,302 Calories to separate unit weight of phosphorus from phosphate of lime, and leave free lime. In a furnace making a pig iron with several per cent. of phosphorus, this item becomes quite large.

Calcium occurs in the slag as CaS, its reduction from lime requiring

(Ca, O) = 130,500 Calories = 3,263 Calories per kg. Ca.

Other elements than the above rarely occur in pig iron in notable quantity. If rare ones occur, their heat of reduction can be sought in thermochemical tables. Those of tungsten, titanium, molybdendum and chromium are, however, not at present known.

(12) *Decomposition of moisture in the blast.* This is to be

counted as vapor of water, the heat required to decompose, which is:

$$(H^2, O) \text{ vapor} = 58{,}060 \text{ Cal.} = 3{,}226 \text{ Cal. per kg. } H^2O.$$
$$= 29{,}030 \text{ " " } H^2.$$

It is not correct to allow here for the sensible heat in this water vapor coming in with the hot blast, because that heat should go on the other side of the balance sheet as heat delivered to the furnace. Neither is it correct to subtract the heat of combination of the oxygen of this moisture with carbon to form CO at the tuyeres; because, although that combination actually does take place, yet the heat thereby evolved properly belongs also on the other side of the balance sheet, and is there properly taken care of as part of the heat of oxidation of carbon in the furnace.

Problem 57.

(Data partly from paper by the author, Transactions American Institute of Mining Engineers, 1905).

A blast furnace running on Lake Superior ore has the following charges, per 100 of pig iron produced:

Hematite ore: 177.6; composition	H^2O	—10.0 per cent.
	SiO^2	—10.0 "
	Al^2O^3	— 3.5 "
	Fe^2O^3	—76.5 "
Limestone: 44.4; composition	SiO^2	— 5.0 "
	MgO	— 4.8 "
	CaO	—47.6 "
	CO^2	—42.6 "
Coke: 95.8;composition	SiO^2	— 5.3 "
	CaO	— 5.3 "
	H^2O	— 1.0 "
	C	—88.0 "
Pig iron produced: 100; composition	Si	— 1.0 "
	C	— 4.0 "
	Fe	—95.0 "
Gases produced: composition dry:	CO^2	—13.0 " vol.
	CO	—22.3 "
	N^2	—64.7 "

Blast used: Contained 5.66 grains of moisture per cubic foot of dry air, at 24° C. = 75° F.
Charges in pounds: Coke, 10,200; ore, 20,000; stone 5,000.
Product per day: Pig iron, 358 tons = 801,920 pounds.
Coke used per day: 768,626 pounds.
Temperature of blast 720° F. = 382° C.
Temperature of waste gases = 538° F. = 281° C.
Displacement of blowing engines = 40,000 ft.^{3} per min.
Heat in one unit of pig iron = 325 Calories.
Heat in one unit of slag = 525 Calories.
Cooling water, per day, heated 50° C. = 300,000 gallons.

Required: (1) The volume of gases per 100 kg. of pig iron
(2) A balance sheet of materials entering and leaving the furnace, per 100 unit of pig iron.
(3) The volume and weight of blast per 100 kg. of pig iron.
(4) The efficiency of the blowing plant.
(5) The heat balance sheet of the furnace.
(6) The proportion of the fixed carbon of the fuel burnt at the tuyeres.
(7) The proportion of the whole heat generated at the tuyeres.
(8) The proportion of the iron reduced in the furnace which is reduced by solid carbon from FeO.
(9) The theoretical maximum of temperature at the tuyeres.
(10) The theoretical maximum if all the moisture were removed from the blast.

Solution: (1) To find the volume of the gases:

Carbon in the coke used 95.8×0.88	= 84.3 kg.
Carbon in the limestone $44.4 \times 0.426 \times \frac{3}{11}$	= 5.2 "
Total carbon entering furnace	= 89.5 "
Carbon in 100 of pig iron	= 4.0 "
Carbon entering gases	= 85.5 "
Carbonous and carbonic oxides in gases	= 35.3 per cent
Carbon in 1 m^3 of dried gas = 0.54×0.353	= 0.19062 kg.
Dry gas per 100 kg. of pig iron = $\frac{85.5}{0.19062}$	= 448.5 m^3. (1)

Dry gas per 100 oz. of pig iron = 448.5 ft.³

Dry gas per 100 pounds of pig iron = 448.5 $\times$ 16 = 7176.0 "

Dry gas per 2240 pounds of pig iron = 7176.0 $\times$ 22.4 = 160,742 "

$$\text{Dry gas per minute} = \frac{160{,}742 \times 358 \text{ (tons)}}{60 \times 24} = 39{,}962 \text{ "}$$

(2) BALANCE SHEET OF MATERIALS, PER 100 OF PIG-IRON.

	Charges		Pig Iron		Slag		Gases	
Ore 177.6	Fe^2O^3	135.6	Fe	95.0	.....		O	40.7
	H^2O	17.8	.....		.....		H^2O	7.8
	SiO^2	17.8	Si	1.0	SiO^2	15.7	O	1.1
Flux 44.4	SiO^2	2.2	.....		SiO^2	2.2	.....	
	CaO	21.1	.....		CaO	21.1	.....	
	MgO	2.1	.....		MgO	2.1	.....	
	CO^2	19.0	.....		.....		CO^2	19.0
Fuel 95.8	C	84.3	C	4.0	.....		C	80.3
	SiO^2	5.3	.....		SiO^2	5.3	.....	
	CaO	5.3	.....		CaO	5.3	.....	
	H^2O	0.9	.....		.....		H^2O	0.9
Blast 422.2	O^2	96.4	.....		.....		O	96.4
	N^2	321.3	.....		.....		N^2	321.3
	H^2O	4.5	.....		.....		H	0.5
							O	4.0
	Total	740.0		100.0		58.0		582.0

The charges are calculated simply from the weights of ore, flux and fuel used, and their percentage composition. The blast is calculated as given in solution of requirement (3).

The 1.0 of silicon in the pig iron requires $1.0 \times (60 \div 28) = 2.1$ parts of SiO^2 to furnish it, leaving 15.7 of unreduced SiO^2 to go into the slag, and 1.1 of oxygen to the gases.

(3) The balance sheet shows that the solid charges furnish to the gases 41.8 of O, 190 of CO^2 and 18.7 of H^2O. The H^2O goes as such into the gases, and therefore its oxygen is not present in the sample of dry gas analyzed. The oxygen in CO^2 is $19.0 \times (32 \div 44) = 13.8$ kg., which added to the 41.8 gives 55.6 of oxygen getting into the gases as CO or CO^2, from the solid charges.

The oxygen in the CO and CO^2 of the gases is to be calculated from the oxygen in unit volume of gas and the total volume of gas produced. The oxygen in 1 cubic meter of gas will be:

$$\text{O in CO} = 0.223 \times \left(0.09 \times \frac{28}{2}\right) \times \frac{16}{28} = 0.16056 \text{ kg.}$$

$$\text{O in } CO^2 = 0.130 \times \left(0.09 \times \frac{44}{2}\right) \times \frac{32}{44} = 0.18720 \text{ "}$$

$$0.34776 \text{ "}$$

A quicker solution is to note that CO^2 represents O^2, its own volume of oxygen, and CO represents O, or half its volume of oxygen, and since 1 cubic meter of oxygen weighs $0.09 \times (32 \div 2) = 1.44$ kilograms, the weight of oxygen required is

$$\left(\frac{0.223}{2} + 0.13\right) \times 1.44 = 0.34776 \text{ kg.}$$

The total oxygen in 448.5 m^3 of gases is therefore

448.5×0.34776	= 156 kg
subtracting that furnished by the solid charges	= 55.6 "
there remains oxygen furnished by blast	= 100.4 "
If the blast were perfectly dry air, its nitrogen would be $100.4 \times (10 \div 3)$	= 334.7 "
and the weight of dry blast	= 435.1 "
and its volume at 0° C. $435.1 \div 1.293$	= 336.5 m^3

The blast, however, is not dry, and the 100.4 kilos. of oxygen includes that brought in by the moisture. The moisture weighs 5.66 grains per cubic foot of measured dried air; it is, therefore, simplest to calculate the oxygen entering the furnace per unit volume of air proper entering. Since 5.66 grains = $5.66 \div 437.5 = 0.01294$ ounces av., the calculation can be made in ounces per cubic foot or kilograms per cubic meter in identical figures as follows:

$$\text{Oxygen in 0.01294 parts of water} = 0.01294 \times \frac{8}{9} = 0.0115$$

$$\text{Oxygen in 1 volume of air proper, at 24° C.} = 1.293 \times \frac{3}{13} \times \frac{273}{273 + 24} = 0.2743$$

$$\text{Sum} = 0.2858$$

The blast received, per 100.4 kg. of oxygen thus received, is therefore, measured dry at 24° C:

$$\frac{100.4}{0.2858} = 351.8 \text{ cubic meters,}$$

and in cubic feet, per 100.4 pounds of oxygen:

$$\frac{100.4 \times 16}{0.2858} = 5628.8 \text{ cubic feet.}$$

The volume of the moist air containing this will be the volume of assumed dried air plus the volume of the water vapor. The latter is, per unit volume of dried air:

$$0.01294 \div \left(0.09 \times \frac{18}{2} \times \frac{273 + 24}{273}\right) = 0.01738$$

and the volume of moist air received, at 24°, is, therefore,

$$351.8 \times 1.01738 = 357.9 \text{ cubic meters.}$$

Or $5628.8 \times 1.01738 = 5726.6$ cubic feet.

The weights of water, oxygen and nitrogen received per 100 of pig iron are (as already given on the balance sheet):

H^2O	$0.01294 \times 351.8 =$	4.52 kg.
O^2	$0.2743 \times 351.8 =$	96.4 "
N^2	$0.9143 \times 351.8 =$	321.3 "

And the volumes of these, considered theoretically at 0° C. and standard pressure, per 100 kg. of pig iron made:

H^2O vapor	$4.52 \div 0.81 =$	5.6 cubic meters.
Air	$417.7 \div 1.293 =$	322.8 " "
	Sum =	328.4 " "

There are several other modifications of this solution which will suggest themselves to anyone who studies out the question, but while half a dozen ways may be equally correct, that one is logically to be preferred which is most easily understood and is the shortest. One solution, however, based on volume relations, is well to know. Water vapor, H^2O, represents half

its volume of contained oxygen, while air has 0.208 oxygen. The cubic foot of dried air at 24° C. was accompanied by

$$0.01294 \div 0.81 \times \frac{273+24}{273} = 0.0174 \text{ cubic foot}$$

of moisture, which was removed in making the test. The oxygen per cubic foot of dry blast was, therefore, at 24° C.:

O as H^2O	$= 0.0174 \div 2$	$= 0.0087$	cubic foot.
O^2 as air	$= 1.0000 \times 0.208 =$	0.2080	" "
		0.2167	" "

Weight of this oxygen:

$$1.44 \times \frac{273}{273+24} \times 0.2167 = 0.2868$$

And volume of dry blast, at 24°, per 100 of pig iron:

$$\frac{100.4}{0.2868} = 350.1 \text{ cubic meters.}$$

The difference of about 0.4 per cent between this and the previously-calculated result is due to the figures not being carried out to a sufficient number of decimal places.

(4) *The efficiency of the blowing plant* is found by calculating the volume of air and moisture received by the furnace per minute, calculated to 24° C. = 75° F., and comparing this with the piston displacement of 40,000 cubic feet per minute.

Volume of moist air received, at 24° C., per 100 lbs. of pig iron made	$= 5726.6$ ft.^{3}
Volume per day $= 5726.6 \times 8019.2$	$= 45{,}922{,}750$ ft.^{3}
Volume per minute $= 45{,}922{,}750 \div 1440$	$= 31{,}891$ "
Efficiency of blowing plant $\frac{31{,}890}{40{,}000}$	$= 79.7$ per cent. (4)

(5) *The heat balance sheet* is based for most of its data upon the balance sheet of materials, the calculations already made and the additional data given in the statement.

The balance sheet shows 80.3 kilos. of carbon oxidized in the furnace. Of this, the amount oxidized to CO and remain-

ing as such in the gases is obtained from the amount of CO in the gases, as follows:

C in CO = $448.5 \times 0.223 \times 0.54 = 54.0$ kg.
C oxidized to CO^2 is therefore $80.3 - 54 = 26.3$ kg.

The heat in hot blast is calculated from its volume assumed to be at 0° C., and already calculated, viz.; 322.8 cubic meters of air proper and 5.6 cubic meters of water vapor, with mean specific heats per cubic meter between 0° and 382° C. of 0.313 and 0.40 respectively.

The heat of formation of the pig iron may be taken from the amount of carbon in the iron, as 705 Calories per kilogram of carbon, and that of silicon omitted from consideration.

The heat of formation of the slag, since it contains 29.5 of silica and alumina to 28.5 of lime and magnesia, may be taken as 150 Calories per unit of silica and alumina.

The total heat received and generated, and to be accounted for, in the furnace, is therefore, per 100 kg. of pig iron:

Carbon to CO 54.0×2430	= 131,220	Calories.
Carbon to CO^2 26.3×8100	= 213,030	"
In H^2O vapor $5.6 \times 0.40 \times 382$ In air proper $322.8 \times 0.313 \times 382$	= 39,385	"
Solution of C in iron 4×705	= 2,820	"
Formation of slag 29.5×150	= 4,425	"
Total	= 390,880	"

The items of heat distribution are 325 Calories in each kilogram of pig iron, 525 Calories in each kilogram of slag, heat in the waste gases at 281°, heat in cooling water, lost by radiation and conduction (by difference), evaporation of the moisture in charges, expulsion of CO^2 from carbonates, decomposition of moisture of blast, reduction of silicon and iron.

Reduction of Fe	95 kg. $\times$ 1,746	= 165,870	Calories.
Reduction of Si	1 " $\times$ 7,000	= 7,000	"
Expulsion of CO^2 from $CaCO^3$	16.7 " $\times$ 1.026	= 18,666	"
Expulsion of CO^2 from $MgCO^3$	2.3 " $\times$ 666		
Evaporation of H^2O	18.7 " $\times$ 606.5	= 11,342	"

Heat in waste gases:

N and CO 400 $m^3 \times 0.3106$ CO^2 58.3 $m^3 \times 0.446$ H^2O 23.1 $m^3 \times 0.382$	$\times 281°$	= 43,836	"
Decomposition of moisture of blast:			
H^2O 4.5 kg. $\times (29{,}040 \div 9)$		= 14,511	"
Heat in slag 58 kg. $\times 525$		= 30,450	"
Heat in pig iron 100×325		= 32,500	"
Heat in cooling water (300,000 gallons per diem) $300{,}000 \times 8.3$ (lbs.) $\times 50° \div 8019.2$		= 15,525	"
Loss by radiation and conduction (difference)		= 51,180	"
	Total	= 390,880	" (5)

(6) *The proportion of the fixed carbon burned at the tuyeres* is obtained by calculating the weight of carbon which the oxygen entering at the tuyeres could oxidize to CO, as follows:

Oxygen entering at the tuyeres	=	100.4 kg.
Carbon burned to CO $= 100.4 \times \frac{12}{16}$	=	75.3 "
Fixed carbon charged	=	84.3 "
Proportion burned at tuyeres	=	89.3 per cent.

A more just proportion is that between the carbon burned at the tuyeres and the total fixed carbon oxidized, because the fixed carbon which carbonizes the iron cannot be oxidized under any circumstances. This proportion in this furnace is:

$$\frac{75.3}{84.3 - 4.0} = 93.8 \text{ per cent.} \qquad (6)$$

indicating a very fair approximation to Grüner's ideal working. If we make the further allowance, that the silicon in the pig iron is necessarily reduced by solid carbon, and that therefore the solid carbon needed to reduce the 1 kilogram of silicon $[1 \times (24 \div 28)]$ is in no case available for combustion at the tuyeres, we have the approach to Grüner's ideal working measured by the ratio

$$\frac{75.3}{80.3 - 0.9} = 94.8 \text{ per cent.}$$

in spite of which, however, the furnace is not doing very good work.

(7) The proportion of the heat requirement generated or available at or about the tuyeres is determined as follows:

Combustion of C to CO = 75.3×2430	= 182,979	Calories.
Heat in hot blast	= 39,385	"
Formaton of pig iron	= 2,820	"
Formation of slag	= 4,425	"
Total	= 229,609	"
Against which must be charged heat required to decompose moisture of blast	= 14,511	"
Leaving net heat available	= 215,098	"
which is $215{,}098 \div 390{,}880$	= 55	per cent.

of the total heat generated and available in the furnace.

Another way in which it is sometimes put, is that the oxidation of carbon to CO or CO^2 furnishes a certain amount of heat to the furnace (346,250 Calories in this case), of which a certain amount is generated by combustion at the tuyeres (182,979 Calories), making the ratio thus considered, in this case, 53 per cent.,—which is almost the same figures as above, but not so significant, since it is illogical to consider the heat brought in by the hot blast as not being available heat for doing work in the tuyere region.

(8) The proportion of iron reduced by solid carbon is found by finding how much carbon is used up in that reduction.

Fixed carbon charged	= 84.3	kg.
Fixed carbon carbonizing the pig iron	= 4.0	"
Fixed carbon oxidized in the furnace	= 80.3	"
Fixed carbon oxidized by the blast	= 75.3	"
Fixed carbon oxidized above the tuyeres	= 5.0	"
Carbon needed to reduce 1 kg. silicon	= 0.9	"
Carbon used for reducing FeO	= 4.1	"
Amount of Fe, thus reduced $= 4.1 \times \frac{56}{12}$	= 19.1	"

Proportion of the total Fe, thus reduced

$$= \frac{19.1}{95} = 20 \text{ per cent.} \qquad (8)$$

(9) The maximum temperature of the gases in the region of the tuyeres is that temperature to which the heat there available will raise the products of combustion. This question is best resolved by simply considering the combustion of 1 kilogram of carbon, evolving 2430 calories, while the heat in the hot carbon itself just before it is burnt, and that in the hot blast required, will also exist as sensible heat in the products,—the whole diminished by the heat necessary to decompose the water vapor blown in.

Since, per 75.3 kg. of carbon burned at the tuyeres there enter 5.6 m^3 of water vapor and 322.8 m^3 of air proper, measured at 0°, the volume of blast per kilogram of carbon oxidized at the tuyeres is

H^2O $5.6 \div 75.3 = 0.0738\ m^3 = 0.0598$ kg.
Air $322.8 \div 75.3 = 4.2869\ m^3$

The products of the combustion are, per kg. of carbon burned:

CO $22.22 \div 12$	= 1.8519	cubic meters.
N^2 $321.3 \div 1.26 \div 75.3$	= 3.3865	" "
H^2 equal to H^2O decomposed	= 0.0738	" "
Total	= 5.3122	" "

The heat available to raise their temperature is:

Heat of combustion of 1 kg. carbon	= 2430 Calories.
Heat in hot blast = $39{,}385 \div 75.3$	= 523 "
Heat in hot carbon at t° (or very nearly)	= 0.5t−120 "
Less heat absorbed in decomposing steam $14{,}511 \div 75.3$	= 193 "
Net heat available in gaseous products	$= 2640 + 0.5t$ Cal

Calorific capacity of gaseous products

$$= 5.3122\ (0.303t + 0.000027t^2)$$

Therefore $5.3122\ (0.303t + 0.000027t^2) = 2640 + 0.5t$

Whence $t = 1910°$ (9)

This represents the absolute maximum of temperature which the gaseous products formed at the tuyeres can possess.

(10) If all the moisture were removed from the blast, the heat available would be:

By combustion of 1 kg. carbon = 2430 Calories.
Heat in 4.4685 m^3 of dry air at 382° C.
$= 4.4685 \times 0.313 \times 382$ = 574 "
Heat in 1 kg. of carbon at t° = 0.5t − 120"
Net heat available in gaseous products = 0.5t + 2884 Cal.
Calorific capacity of gaseous products
$= 5.3976\ (0.303t + 0.000027t^2)$
Therefore $5.3976\ (0.303t + 0.000027t^2) = 2884 + 0.5t$
Whence $t = 2018°$ (10)

It is to be noted that this is 108° C. = 194° F. higher than with moist blast; and while the slag and iron in passing through this zone of high temperature will not reach this maximum temperature, yet they would be heated approximately 100° C. higher when using dry blast, if all other conditions were kept constant.

N. B.—In working this problem, the metric measurements and English measures have been purposely used interchangeably, in order that readers may understand better that if weights are taken in pounds and the heat unit is the pound Calorie (1° C.), the same numbers represent a solution in either system. When volumes are concerned, cubic feet and ounces, or ounce calories, have practically the same numerical expression as cubic meters and kilograms or kilogram calories.

CHAPTER V.

THE RATIONALE OF HOT-BLAST AND DRY-BLAST.

Problem 58 (for practice).

The blast furnace of Problem 57 had its blast dried before using, to the extent of leaving on an average 1.75 grains of moisture per cubic foot of air proper, at − 5° C., in the air pumped. The composition of the ore, limestone and coke used was unchanged, also that of the pig iron made. The weights charged per 100 of pig iron were: Ore 177.6, flux 44.4, fuel 77.0, and the blast used calculates out oxygen 76.5, nitrogen 255.0, moisture 1.0. Analysis of gases: CO 19.9, CO^2 16, N^2 64.1 per cent. Product per day 447 tons. Temperature of gases 191° C., of blast 465° C. Piston displacement (air at − 5° C.) 34,000 cubic feet per minute. Assume heat in pig iron and slag same as before, in cooling water 20 per cent. greater per day.

Required.—(1) The volume of gases per 100 kg. of pig iron made.

Answer.—Measured dry, 355.9 m^3.

(2) A balance sheet of materials entering and leaving the furnace, per 100 units of pig iron. (See table on page 281.)

(3) The volume of blast per 100 kg. of pig iron.

Answer.—252.9 m^3 at − 5° C.

(4) The efficiency of the blowing plant.

Answer.—82.3 per cent.

(5) The heat balance sheet of the furnace, per 100 of pig iron.

Developed.

Carbon to CO	92,950	Calories.
Carbon to CO^2	206,955	"
Heat in hot blast	37,850	"
Solution of carbon in iron	2,820	"
Formation of slag	4,260	"
Total	344,835	"

Distributed.		
Reduction of iron	165,870	Calorics.
Reduction of silicon	7,000	"
Expulsion of carbonic oxide (CO^2)	18,666	"
Evaporation of moisture of charges	11,342	"
Heat in waste gases	23,799	"
Decomposition of moisture of blast	3,225	"
Heat in slag	29,820	"
Heat in pig iron	32,500	"
Heat in cooling water	14,922	"
Lost by radiation and conduction (diff.)	37,791	"
	344,835	"

(6) Compare the heat items which are substantially different for the furnace run by moist and dried blast.

	Moist Blast.	*Dried Blast.*
Combustion of C to CO	131,220	92,950
Heat in waste gases	43,836	23,799
Decomposing moisture in blast	14,511	3,225
Loss by radiation and conduction	51,180	37,791

It may be noticed, that using moist blast too much carbon was burnt to CO at the tuyeres; the chief item of economy with dried blast is the ability to get along with less. The smaller total amount of gases, particularly nitrogen, accounts for the lower temperature of the waste gases, with dried blast. The direct saving by reason of decomposition of the moisture is the smallest item of economy. The reduced losses by radiation and conduction are mainly because of the faster rate of running, these losses being nearly constant per day. The ratio of these losses is found to be 0.74, whereas, the inverse ratio of the pig iron productions per day was 0.79.

(7) Calculate the carbon burnt at the tuyeres, the proportion of the carbon available thus consumed. Compare these items with those of the furnace on moist blast.

	Moist Blast.	*Dried Blast.*
Carbon burnt at tuyeres	75.3	58.05
Total fixed carbon charged	84.3	67.8
Proportion burnt at tuyeres	89.3	85.6
Fixed carbon really available	79.4	62.9
Proportion burnt at tuyeres	94.8	92.3

(In some charcoal furnaces of low heat requirement, *i.e.*, with pure ores and fuel, as little as 37 parts of carbon is burned at the tuyeres per 100 of pig iron produced, which represents, moreover, only 70 to 75 per cent. of the available fixed carbon in these furnaces.)

	Charges.		Pig Iron.		Slag.		Gases.	
Ore 177.6	Fe^2O^3	135.7	Fe	95.0	.....		O	40.7
	H^2O	17.8	.....		.....		H^2O	17.8
	SiO^2	17.8	Si	1.0	SiO^2	15.7	O	1.1
	Al^2O^3	6.3	.....		Al^2O^3	6.3	.....	
Flux 44.4	SiO^2	2.2	.....		SiO^2	2.2	.....	
	CaO	21.1	.....		CaO	21.1	.....	
	MgO	2.1	.....		MgO	2.1	.....	
	CO^2	19.0	.....		.....		CO^2	19.0
Fuel 77.0	C	67.8	C	4.0	.....		C	63.8
	SiO^2	4.2	.....		SiO^2	4.2	.....	
	CaO	4.2	.....		CaO	4.2	.....	
	H^2O	0.8	.....		.....		H^2O	0.8
Blast 332.5	O^2	76.5	.....		.....		O	76.5
	N^2	255.0	.....		.....		N	255.0
	H^2O	1.0	.....		.....		H	0.1
							O	0.9
	Totals	631.5		100.0		55.8		475.7

(8) The proportion of the whole heat requirement available in the region of the tuyeres.

Answer.—**53** per cent.

(9) The proportion of the iron in the furnace which is reduced by solid carbon from FeO.

Answer.—**23.8** per cent.

(10) The theoretical maximum of temperature at the tuyeres.

Answer.—**1965°** C.

Hot Blast.

For several centuries blast furnaces were run by charcoal as fuel and with cold blast. How great the variations in temperature of the cold blast may be, can be inferred from the experience of a furnace manager in the Urals, Russia, who noted temperatures of the air nearly 40° C. in the summer and − 60° C. in the winter. Assuming an average temperature of 0° C. for unheated blast, burning charcoal to CO, the theoretical maximum of temperature before the tuyeres can be calculated as follows:

Heat generated by combustion		2430 Calories
Heat in hot carbon being burnt	0.5t −	120 "
Volume of CO and N^2 formed		5.3795 cubic meters

$$\text{Temperature} = \frac{2310 + 0.5t}{5.3944\ (0.303 + 0.000027t)}$$

Whence $t = 1678°$

This does not mean that the pig iron and slag will be carried to this temperature, any more than if a locomotive could run alone 90 miles an hour it could therefore pull a train of cars that fast. The hot gases, CO and N^2, are at the start at this temperature, and as they ascend and come in contact with the descending iron and slag, these are raised to temperatures approximating towards, but always lower than, the above. In fact, the temperature to which the iron and slag is raised depends on the relative quantities of iron and slag to fuel burnt, and the speed with which the furnace is worked.

If the blast is heated, its sensible heat is simply added to the numerator of the above expression. We can easily find out how much sensible heat the 4.4685 cubic meters of air brings in, at any temperature desired [$Q = 4.4685\ (0.303t + 0.000027t^2)$], and then solve the quadratic anew. We thus find

Temp. of Blast.	*Heat in Blast.*	*Theoretical Temp.*
0° C.	— Calories	1678° C.
100° "	137 "	1762° "
200° "	276 "	1845° "
300° "	417 "	1929° "
400° "	561 "	2012° "
500° "	707 "	2096° "
600° "	856 "	2180° "

Temp. of Blast.	*Heat in Blast.*	*Theoretical Temp.*
700° C.	1007 Calories.	2265° C.
800° "	1160 "	2350° "
900° "	1316 "	2435° "
1000° "	1475 "	2520° "

The heating of the blast thus raises the maximum temperature available some 85° C. for each 100° C. to which the blast is heated. It not only increases the temperature available, but also the number of heat units, thus increasing both the quantity and the intensity of the heating in the tuyere region. Of these two items of increase, that of the intensity factor is the most important, since it regulates the rapidity of transfer of heat to the charge and the efficiency and speed of the smelting action of the furnace.

Dried Blast.

Each kilogram of water vapor decomposed absorbs $29040 \div 9 = 3227$ Calories, which would not be needed if the 0.67 kilo. of carbon thus employed was oxidized by air instead of by moisture. Per kilogram of carbon oxidized by water vapor, there is absorbed $58{,}080 \div 12 = 4{,}840$ Calories, while this kilogram of carbon can only furnish 2430 Calories in becoming CO, leaving a net absorption of 2410 Calories per kilogram of carbon thus burned, against which, however, can be credited the heat in the kilo. of carbon burned and the sensible heat in the water vapor itself; the former is $0.5t - 120$, and the latter can be calculated from the volume of the water vapor, 1.8519 cubic meters. We thus have, per kilogram of carbon thus oxidized:

Temperature of Water Vapor.	*Heat in Moisture.*	*Heat in Products.*
100°	66 Calories	$0.5t - 2460$ Calories
200°	137 "	$0.5t - 2393$ "
300°	214 "	$0.5t - 2316$ "
400°	296 "	$0.5t - 2234$ "
500°	384 "	$0.5t - 2146$ "
600°	478 "	$0.5t - 2042$ "
700°	577 "	$0.5t - 1953$ "
800°	682 "	$0.5t - 1848$ "
900°	792 "	$0.5t - 1738$ "
1000°	907 "	$0.5t - 1623$ "

Since the heat in the carbon burnt $(0.5t - 120)$ can never equal numerically 1623, it is seen that under no circumstances can the water vapor do anything but diminish the quantity of heat available at the tuyeres, while the products of its decomposition CO and H^2 increase the volume of the products and so diminish still further the intensity of temperature attainable.

The best way to determine the amount of moisture in the air is to draw it through a tube containing concentrated sulphuric acid, measure the quantity of dry air drawn through, and weigh the amount of moisture caught by the tube. This gives the weight of moisture *accompanying* unit volume of dry air (not weight of moisture in unit volume of moist air). Determinations by the wet and dry bulb thermometers, the whirled psychrometer, humidity gauges, etc., are none of them so reliable as the above described method, which is direct, simple and accurate. The results may be obtained in grains per cubic foot of dry air or milligrams per liter. The best way to express them, for further use, is in ounces avoirdupois per cubic foot, or kilograms per cubic meter. The first is obtained by dividing the number of grains by 437.5, the second by dividing the milligrams per liter by 1000. The numbers thus obtained are practically identical in the two systems.

The theoretical temperatures attainable with moist blast of varying degrees of moisture and heated to various temperatures are obtained by applying the previously explained principles. We have already calculated the temperature obtained by burning carbon with dry air of various temperatures. We have also calculated a table of the deficit of heat available produced by the entrance of 1.5 kilos. of water vapor (which would oxidize 1 kilo. of carbon and produce 1.8519 cubic meters of CO and H^2). We are, therefore, prepared to calculate a table of the maximum temperature attainable using blast of any degree of humidity heated to any practical temperature. Before giving the table we will run through the details of one calculation, to make clear the method employed.

Illustration.—What is the theoretical maximum temperature using air which carries normally 10 grams of moisture per cubic meter of dry air, reduced to standard conditions (*i.e.*,10 grams per 1.293 kilograms of dry air), and heated to 500° C.?

It takes 3.5275 cubic meters of dry air at standard condi-

tions to burn 1 kilogram of carbon. If dry, and at 500°, there is 2430 Calories generated by combustion, 707 Calories in the dry air used, $0.5t - 120$ Calories in the hot carbon, and the total heat thus at hand raises the 5.3944 cubic meters of products to the temperature of 2096° C., as is determined by solving the equation

$$t = \frac{2430 + 707 + (0.5t - 120)}{5.3944\ (0.303 + 0.000027t)} = 2096°$$

As modified by the moisture, the 4.4685 cubic meters of dry air would be accompanied by 44.685 grams of moisture, or 0.044685 kg., which would oxidize two-thirds of its weight of carbon, or 0.02979 kg. of carbon, which would contribute to the heat available $0.02979\ (0.5t - 2146)$ Calories, making a contribution of $0.015t - 64$ Calories to the numerator of above equation. The products of combustion will be increased by H^2 and CO equal in volume to twice the volume of the moisture, or $2 \times 0.044685 \div 0.81 = 0.1102$ cubic meters, the mean specific heat of which goes into the denominator. We then have

$$t = \frac{3017 + 0.5t + 0.015t - 64}{(5.3944 + 0.1102)\ (0.303 + 0.000027t)} = 2030°$$

Another method of solution, not using the previously calculated tables but based entirely on first principles, is to base the whole calculation on the use of 1 cubic meter of dry air, with its accompanying moisture, as follows:

Oxygen present in 1 m^3 dry air $= 1{,}293 \times 3/13$	$=$	0.2984 kg.
Oxygen present in the moisture $= 0.010 \times 8/9$	$=$	0.0089 "
Total	$=$	0.3073 "
Carbon consumed $= 0.3073 \times 0.75$	$=$	0.2305 "
Volume of moisture $= 0.010 \div 0.81$	$=$	0.0123 m^3
Volume of oxygen in dry air	$=$	0.2078 "
Volume of products from dry air $= 1.0000 + 0.2078$	$=$	1.2078 "
Volume of products from moisture $= 2 \times 0.0123$	$=$	0.0246 "
Total volume of products	$=$	1.2324 "
Heat of combustion of carbon $= 0.2305 \times 2430$	$=$	560 Cal.
Heat in carbon at t° $= 0.2305 \times (0.5t - 120)$	$=$	$0.1152t - 28$ "

Heat in dry air at 500° = $1 \times [0.303 + 0.000027 (500)] 500$ = 158 Cal.
Heat in moisture at 500° = $0.0123 [0.34 + 0.00015 (500)]$ = 3 "
Heat absorbed in decomposing moisture = 0.0123×2614 = − 32 "

Whence results the equation

$$t = \frac{0.1152t + 661}{0.2324\ (0.303 + 0.000027t)} = 2030°$$

By applying either of the two methods of calculation explained, the temperatures in the following table are obtained:

THEORETICAL TEMPERATURES BEFORE THE TUYERES

MOISTURE. { Grams per cubic meter of dry air reduced to 0° C.
Grains per cubic foot of dry air reduced to 0° C.

Grams	5.00	10.00	15.00	20.00	25.00	30.00	35.00	40.00
Grains.	2.19	4.38	6.57	8.75	10.94	13.13	15.32	17.50
Blast.								
40°	1678°	1647°	1615°	1573°	1536°	1507°	1471°	1443°
100°	1723	1692	1666	1627	1587	1548	1526	1496
200°	1807	1776	1751	1712	1673	1636	1612	1584
300°	1892	1861	1837	1800	1760	1725	1700	1673
400°	1976	1945	1921	1885	1846	1813	1786	1760
500°	2061	2030	2007	1970	1933	1902	1874	1848
600°	2146	2115	2093	2055	2020	1991	1962	1936
700°	2232	2201	2178	2144	2108	2080	2050	2025
800°	2318	2287	2264	2227	2195	2169	2138	2114
900°	2404	2373	2351	2313	2282	2257	2226	2203
1000°	2490	2459	2437	2399	2369	2345	2314	2292

The calculations show that the temperature before the tuyeres may vary as much as 235° C. = 423° F., from change in the moisture of the air, from dryness to warm air saturated with moisture.

CHAPTER VI.

PRODUCTION, HEATING AND DRYING OF AIR BLAST.

This is a subject intimately related to the running of iron blast furnaces, and incidentally related more or less to all classes of metallurgical operations. The principles involved are those of physics—mechanical and thermal—and when once thoroughly understood can be used for the most various classes of metallurgical problems.

Production of Blast.

There are two different principles upon which air is compressed, represented by the fan and the piston machines. The first is constant in its operation, the second intermittent, the first draws in and expels a continuous current of air, the second draws in a given quantity of air, compresses it and expels it. Measuring the work done by the difference in static conditions of the compressed and of the uncompressed air, the work actually done is a fixed and calculable quantity, independent of what type of machine performs it. During the compression, heat is generated, and the mechanical work done includes the mechanical equivalent of the heat thus generated. This is allowed for in the well-known formula for adiabatic compression:

$$\text{Work} = \frac{\gamma}{\gamma - 1} V_0 p_0 \left[\left(\frac{p_1}{p_0} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right]$$

in which

γ = the ratio of the specific heat of air at constant pressure to that at constant volume = 1.408.
V_0 = the volume of the uncompressed air.
p_0 = the tension of the uncompressed air.
p_1 = the tension of the compressed air.

If we use the value of $\gamma = 1.408$, the coefficient $\frac{\gamma}{\gamma - 1}$ becomes 3.45, and $\frac{\gamma - 1}{\gamma} = 0.29$. If we then use the other di-

mensions in feet and pounds, the resulting work done will be in foot-pounds; if we use meters and kilograms, in kilogram-meters. The element of time does not enter into this equation, the work actually done is the same for compressing a given amount of air, and is independent of the time. If I lift a kilogram 1 meter high, the same amount of work is done whether I lift it in 1 minute or in 1 second, the *rate of doing work* would be, however, sixty times as great in the last instance as in the first, but the actual amount of work accomplished is the same in each case. If, therefore, we use in the formula the volume of air entering the compressor per minute, the result will give the work done per minute; if we use the volume per second we get the work done per second. If we wish to transpose the work done into horse-power, we bear in mind that a horse-power is understood in English units as 33,000 foot-pounds of work done per minute, and in the metric system as 75 kilogram-meters of work done per second.

In applying the formula we may further notice that $\frac{p_1}{p_0}$ expresses the ratio of compression; that is, by how many times the tension of the original air is increased. If air at one atmosphere tension (such as the air we usually have to breathe) is compressed to two atmospheres tension, the ratio of compression is 2; if air entered a machine at two atmospheres tension and was therein compressed to four atmospheres, the ratio of compression would be likewise 2, and the work done (for a given quantity of air) the same as before. The effective pressure, as shown on a gauge, is the *difference* between these two tensions: it is not p_1. It is highly important that this point be held clearly in mind. The tension of the uncompressed air is its barometric pressure, as measured against a vacuum; the tension of the compressed air is likewise its pressure as measured against a vacuum; the effective pressure of the compressed air is the difference between these two tensions; the tension of the compressed air is, therefore, (by transposition) equal to the barometric pressure of the uncompressed air plus the effective pressure of the compressed air, *i.e.*, plus the gauge pressure. Never use the effective pressure of the compressed air as p_1, but always add to it the barometric pressure of the uncompressed air p_0 for the correct value of p_1.

Regarding the volume of uncompressed air, V_0 is its volume measured at the pressure P_0, *i.e.*, the actual volume of uncompressed air at its actual tension. If more convenient, however, we may use the volume of this air measured at standard barometric pressure, if we multiply it by p_0, the standard pressure. Thus, if we know the volume of uncompressed air measured at one atmosphere standard tension, we may use for the p_0 immediately following it the standard pressure 10.334 (kilos. per square meter), or 2,120 (pounds per square foot). By the law of the reciprocal nature of volume and pressure, the product thus obtained is the same as would be found by multiplying the volume of the same air at any other pressure by that pressure ($V_0 p_0 = V_1 p_1 = V^2 p^2$, etc.). Whatever pressure we use in getting the product $V_0 p_0$, however, we must use only the actual tension of the uncompressed air as the denominator in getting the ratio of compression ($p_1 \div p_0$).

Problem 59.

A blast furnace requires 2,615 cubic meters of air, measured at − 5° C., for every metric ton of pig iron made. Assuming outside barometric pressure 735 millimeters of mercury column, the efficient pressure of the compressed blast to be 1.0 kilogram per square centimeter (as measured in a blast regulating reservoir), a mechanical efficiency of the blowing engine of 90 per cent., of delivery of blast 82.3 per cent., and output 447 tons per day:

Required:

(1) The ratio of compression of the blast.

(2) The piston displacement per ton of pig iron made.

(3) The work of the blowing cylinders, per ton of iron made.

(4) The gross or indicated horse-power of the steam cylinders.

Solution:

(1) The effective pressure being 1.0 kilogram per square centimeter, represents $\frac{1.0000}{1.0334} \times 760 = 735$ millimeters of mercury. But the uncompressed air is at 735 mm. barometric tension, therefore, the total tension of the compressed air, p_1, is 1470 mm. of mercury, and the

$$\text{Ratio of compression} = \frac{1470}{735} = 2.0 \qquad (1)$$

(2) Piston displacement per metric ton of pig iron:

$$\frac{2615}{0.823} = \textbf{3165} \text{ cubic meters.} \qquad (2)$$

$$= \textbf{111,560} \text{ cubic feet.}$$

(3) The volume displaced must be the basis of calculating the power required, since subsequent losses of air (100 − 82.3 = 17.7 per cent.) do not affect the work done in the blowing cylinder. This volume is 3,165 cubic meters, representing that volume of uncompressed air at − 5° C. and 735 mm. pressure. The initial temperature of the air does not affect the work to be done, and we can either use its volume at 735 mm. tension or correct this to 760 mm. tension, just as we chose. If we consider the volume at 735 mm. tension, then the product of volume and pressure is

$$Vp = 3{,}165 \times \left(10{,}334 \times \frac{735}{760}\right) = 31{,}755{,}000$$

If we first change the volume to standard pressure, we have

$$V_0 p_0 = \left(3{,}165 \times \frac{735}{760}\right) \times 10{,}344 = 31{,}755{,}000$$

The work done in compression, in the blowing cylinder is, therefore,

$$W = 3.45 \times 3{,}073 \times 10{,}334 \times [2^{0.29} - 1]$$
$$= 109{,}554{,}750 \times [1.2225 - 1]$$
$$= \textbf{24,326,800} \text{ kilogrammeters.} \qquad (3)$$

(4) The steam in the steam cylinders does more mechanical work than would be represented by the compression of air in the blowing cylinders. In this case, we assume 90 per cent. mechanical efficiency, or 10 per cent. mechanical loss. The gross work of the steam is, therefore,

$$24{,}326{,}800 \div 0.90 = 27{,}029{,}800 \text{ kilogrammeters,}$$

or, in horse-power,

$$\frac{27{,}029{,}900 \times 447}{1440 \times 4500} = \textbf{1,865} \text{ horse-power.}$$

This amounts to 4.17 h.p. per metric ton of pig iron made per day.

Measurement of Pressure.

In making calculations of the work done in furnishing blast, as in the preceding problem, it is important to note how the pressure of the compressed air is measured. The real pressure is measured correctly by a pressure gauge only where the air is comparatively at rest, as on a pressure-equalizing reservoir. If the pipe communicating with a gauge is connected with a blast main, in which the velocity of the air is considerable, the pressure recorded will vary greatly with the direction of the end of this tube relative to the direction of the air current. The total pressure of the air in motion is the pressure which it exerts against the sides of the main, plus the pressure which has been used in giving it velocity. If the pressure gauge tube is cut off at right angles to the flow of air in the main, the pressure recorded is even less than the actual static pressure of the air against the sides of the main (because of suction effect), and does not include at all the pressure represented by the velocity. The only way to measure correctly in a main the total pressure which has been impressed upon the blast is to bend the end of the pressure tube until it is parallel with the axis of the main and faces the current of air. The gauge then records the static pressure, plus the velocity head, and gives the proper pressure to use in calculating the work done by the blowing engine. However, it is still preferable to put the gauge on a blast reservoir, if there is one, where the air is nearly at rest and velocity head approximates zero—for the reason that the velocity of air passing through a tube is greatest in the center and least against the walls, and it is difficult to place the pressure tube so as to measure the mean velocity. An approximation to the mean value is found by placing the end of the pressure tube not in the center but at one-third of the radius of the main from the center.

Indicator Cards.

If the blowing engine cylinder can be tested by pressure indicator cards, then a different method of obtaining the work of producing the blast is furnished. The integration of the diagram gives the mean pressure on the piston during the stroke. Expressing this in kilograms per square meter or pounds per square foot, and multiplying by the area of the

piston and the length of the cylinder, we get the work done per stroke; again multiplying by the number of strokes per minute we have the work done per minute, from which is readily obtained the horse-power. These operations are usually combined in the formula:

$$\text{Work} = P \times L \times A \times N$$

If we observe that $L \times A \times N$ is the piston displacement per minute, the formula becomes:

$$\text{Work} = P \times \text{Piston displacement per minute},$$

in which, it must not be forgotten, P represents mean pressure on the piston during the stroke, and is not to be confounded with gauge pressure of the compressed air. Such a formula is, therefore, totally inapplicable to finding the work done by a fan or rotary blower, in which only the final pressure of the compressed air is known. The mistake of so applying it is often made. When only the final pressure of the compressed air is known, the formula for adiabatic compression is the only correct one to use.

It may not be useless to call attention to the fact that when using the formula for adiabatic compression, the raising of the ratio of compression to the 0.29 power has to be done by logarithms:

$$\log. \left[\left(\frac{p_1}{p_2}\right)^{0.29}\right] = \log.\left(\frac{p_1}{p_0}\right) \times 0.29$$

If a table of logarithms is not at hand, a satisfactory approximation may be made by taking the cube root of the ratio, since

$$\sqrt[3]{\left(\frac{p_1}{p_2}\right)} = \left(\frac{p_1}{p_0}\right)^{0.33}$$

Heating of the Blast.

Air blast is commonly heated either continuously, by direct transmission of heat through metal or earthenware pipes, or discontinuously by the heating up of fire-brick surfaces, which are subsequently cooled by the blast. It is not within the province of these calculations to enter into a description of the various types of such hot-blast stoves, but to indicate the principles upon which the metallurgist can base calculations as to the efficiency of such stoves, and thus be prepared to find

out which do the best work, and wherein lie the principal advantages or disadvantages of each type.

The efficiency of a hot-blast stove is measured by the ratio of the heat imparted to the blast to that contained in the air and fuel used and generated by combustion. It is a furnace whose useful effect is the heat imparted to the air, and all other items of heat distribution are more or less necessary losses. The problem is simplest when the stove is a recuperator (continuous type), using solid fuel. Then the item of heat generation is perfectly definite, since the amount of fuel used in a given time can be definitely determined. When the hot-blast stove receives gaseous fuel, however, from a blast furnace, the amount of gas received by the stoves is usually a very uncertain quantity, since only part of all the gas produced by the furnace is used by the stoves, and the question of what fraction is thus used is difficult to determine. In such cases, the usual method of comparing the sizes of the pipes leading gas to the stoves and those carrying gas to boilers, etc., affords but a very uncertain determination, since the draft and consequent velocity of the gas may be very different in the two sets of pipes. In such cases, knowing the total volume of gas produced by the furnace, not only the relative sizes of the hot-blast stove pipes should be noted, but also the relative velocities of the gas currents in the two sets of pipes. Another method is to determine the quantity of chimney gas passing away from the stoves into the chimney flues, by measuring the size of the chimney flue, temperature of the gases and average velocity; given in addition the chemical analyses of the chimney gas and of the furnace gas, the quantity of the latter being used can be calculated, using the carbon in the two gases as the basis of calculation.

Problem 60.

Statement: Air for drying peat in a kiln is heated from 0° C. to 150° C. by an iron pipe stove, the latter consuming dried peat, whose ultimate analysis is:

Carbon	49.70 per cent.
Hydrogen	5.33 "
Oxgyen	30.76 "
Nitrogen	1.01 "
Ash	13.23 "

The calorific power of this peat is 4249, and by the combustion of 92.5 kilograms, 5122 cubic meters of air is heated to the required temperature. The products of combustion pass away from the stove at 200° C., and contain (analyzed dry) 14.8 per cent. of CO^2, and no CO or CH^4 or other gas containing carbon.

Required:

(1) The heat generated in the stove.

(2) The heat in the hot air, and the net efficiency of the stove.

(3) The volume and composition of the products of combustion in the stove.

(4) The heat carried out in the chimney of the stove.

(5) The heat lost by radiation and combustion.

(6) The excess of air used in burning the peat.

(1) Heat generated in the stove:

$4249 \times 92.5 = 393{,}033$ Calories (1)

(2) Heat imparted to the air:

$[0.303 + 0.000027\ (150)] \times 150 \times 5122 = 235{,}907$ "

Net efficiency = **60.0** per cent. (2)

(3) Volume of products of combustion:

Weight of carbon in fuel burnt $-$ $92.5 \times 0.4970 = 45.97$ kilos.

Volume of CO^2 thus produced $-$ $45.97 \div 0.54 = 85.13$ cub. meters

Volume of (dry) gas produced $-$ $85.13 \div 0.148 = 575.20$ " "

Volume of N^2 and O^2 in products $-$ $575.2 - 85.13 = 490.07$ " "

Volume of water vapor in products $-$ $92.5 \times 0.0533 \times 9 \div 0.81 = 54.78$ " "

Percentage composition of products of combustion:

	Moist.	*Dried.*
CO^2	13.5	14.8
N^2 and O^2	77.8	85.2
H^2O	8.7	....

To separate the nitrogen and oxygen would necessitate considerable calculation, and is not required just here, because the two gases have the same heat capacity per cubic meter, and therefore can thermally be reckoned together:

(4) Heat in the chimney gases at 200°:

CO^2	85.13 $m^3 \times 0.4140$	= 35.24
N^2 and O^2	490.07 $m^3 \times 0.3084$	= 151.14
H^2O	54.78 $m^3 \times 0.3700$	= 20.27
		206.65×200 = 41,330 Cal.
		Proportion thus lost = 10.5 P. C. (4)

(5) Loss by radiation and conduction

$100 - (60.0 + 10.5)$ = 29.5 P. C. (5)

(6) The separation of N^2 and O^2 in the products is not easy. It is best based on the consideration that part of these consists of the nitrogen of the air which was necessary for combustion (plus the nitrogen of the fuel) and of the excess air. The first can be calculated, and thus the latter obtained by difference, and then the percentage of air in excess determined. Oxygen necessary for combustion:

C to $CO^2 = 45.97 \times \frac{32}{12}$	= 122.59 kilos.
H to $H^2O = 4.93 \times 8$	= 39.44 "
	162.03 "
Oxygen present in peat 92.5×0.3076	= 28.45 "
Oxygen to be supplied	= 133.58 "
Nitrogen accompanying	= 445.27 "
Air necessary	= 578.85 "
	= 447.7 m^3
Nitrogen from coal, 92.5×0.0101	= 0.93 kilos.
Total nitrogen from coal and necessary air	= 446.2 "
Volume $= 446.2 \div 1.26$	= 354.1 m^3
Total N^2 and O^2 in products	= 490.1 "
Therefore, excess air	= 136.0 "
Percentage of excess air $\frac{136.0}{447.7} = 0.303$	= 30.3 P. C. (6)

Problem 61.

A blast furnace has three hot-blast stoves, two of which are always on gas and one on blast. Per long ton of pig iron produced there issues from the furnace (reduced to standard temperature and pressure):

Nitrogen	81,763	cubic feet
Carbon monoxide	25,383	" "
Carbon di-oxide	20,409	" "
Water vapor	8,230	" "

For the same quantity of pig iron made, 92,330 cubic feet (standard conditions) of air is heated in the stoves from −5° C. to 465° C. The hot gases reach the stoves at 175° C., are there burned by 10 per cent. excess of air at 0°, and the chimney gases resulting (assume perfect combustion) pass out of the stoves at 120° C.

Required:

(1) The net efficiency of the stoves, assuming they receive 25, 30, 35, 40, 45 or 50 per cent. of the gas produced by the furnace.

(2) Assuming that each stove radiates and loses to the ground one-third as much heat as the blast furnace itself (the heat balance sheet of the furnace showed 846,518 pound Calories thus lost per long ton of pig iron produced), what proportion of the whole gas goes to the hot-blast stoves, and what is the net efficiency of the stoves?

Solution:

(1) We will first calculate the efficiency of the stoves, assuming that they received *all* the gas produced, from which datum can then be obtained the efficiency, supposing any assumed fraction of the gas goes to the stoves.

Heat in the blast (−5° to 465°):

$$92{,}330\times[0.303+0.000027\ (465-5)]\times[465-(-5)]$$
$$=92{,}330\ \times 0.31542\times 470 = 13{,}687{,}683 \text{ ounce cal.}$$
$$= 855{,}480 \text{ pound Cal.}$$

Sensible heat in the hot gases (0° to 175°):

N^2 and CO	$107{,}146\times 0.3077$	=	32,969
CO^2	$20{,}409\times 0.4085$	=	8,337
H^2O	$8{,}230\times 0.3763$	=	3,097
Heat capacity per 1°		=	44,403 ounce cal.
		=	2,775 pound Cal.
Heat capacity per 175..	$2{,}775\times 175°$	=	.485,625 " "

Heat generated by combustion:

CO to CO^2 25,383 × 3062	= 77,722,746 ounce cal.
	4,857,672 pound Cal.
Total heat available	= 5,343,297 " "

If the gas were all used in the stoves the efficiency of the latter would be only

$$\frac{855,480}{5,343,297} = 0.160 = 16.0 \text{ per cent.}$$

With smaller proportions of the whole gas used the efficiency of the stoves calculates out as follows:

Using	50	per cent.	of the gas.....	Efficiency	32.0	per cent.
"	45	"	"	"	36.0	"
"	40	"	"	"	40.0	"
"	35	"	"		45.7	"
"	30	"	"	"	53.3	
"	25	"	"	"	64.0	
"	16	"	"	"	100.0	"

(1)

All that the above analysis tells us is, that certainly over 16 per cent. of the gas produced by the furnace must be used by the stoves; but if we can deduce any probable value for the percentage of the gas actually used, such as by measuring the several gas mains and the velocities of the gas in each, we can then reckon out the value of the efficiency of the stoves, with about the same degree of probability. Blast furnaces use from 33 to 60 per cent. of the gas they produce in the stoves. If we assume 50 per cent., in this case, the efficiency of the stoves would be 32 per cent.

(2) There is another way of solving the problem, which is to either measure, calculate or assume the heat lost by radiation and conduction from the stoves; adding to this the heat going out in the products of combustion, and the net heat in hot blast, the sum is the total heat which has been brought into and generated within the stoves. But, all the gas would bring in and generate in the stoves 5,343,297 Calories; we can, therefore, find easily what proportion of all the gas is being used in the stoves. In requirement (2) we are told to assume that the three stoves lost by radiation and conduction

846,518 pound Calories per long ton of pig iron made, an amount equal to that similarly lost by the furnace itself. The heat in the chimney gases, at 120°, can be thus calculated:

Oxygen required $\left(\frac{1}{2}\ CO\right)$	=	12,692	cubic feet
Air required	=	61,017	" "
Excess of air used	=	6,102	" "
Nitrogen of required air	=	48,325	" "
Nitrogen already in gas	=	81,763	" "
Nitrogen in these two items	=	130,088	" "
Chimney products:			
CO^2	=	45,792	" "
H^2O	=	8,230	" "
N^2	=	130,088	" "
Excess air	=	6,102	" "
Heat in chimney gases:			
CO^2 $45,792 \times 0.3964$	=	18,152	ounce cal.
H^2O $8,230 \times 0.3580$	=	2,946	" "
N^2 and air $136,190 \times 0.3064$	=	41,729	" "
Heat capacity per 1°	=	62,827	" "
	=	3,927	pound Cal.
Heat capacity per 120°	=	471,122	" "

If all the furnace gas were burnt in the stoves, 471,122 pound Calories would go up the stove chimneys. But, since only a part of the gas is so used, only a fraction of this amount of heat is lost to the chimneys. If we call X the proportion of the gases used, then 471,122 X will represent the chimney loss, and the total heat requirements of the stoves will be:

Heat in air blast	=	855,480 lb. Cal.
Heat in chimney gases	=	471,122 X "
Radiation and conduction	=	846,518 "
Total	=	1,701,998 + 471,122 X lb. Cal.

The proportion of the total gases needed to supply this, X, is

$$\frac{1,701,998 + 471,122\ X}{5,343,297} = X$$

whence

$$X = 0.349 = 34.9 \text{ per cent.} \qquad (2)$$

and the net efficiency of the stoves is

$$\frac{855{,}480}{5{,}343{,}297 \times 0.349} = \frac{855{,}480}{1{,}864{,}812} = \mathbf{45.9}\text{ per cent.} \qquad (2)$$

Arithmetically, the finding of X can be simplified, perhaps, by considering that the chimney loss represents in any case $471{,}122 \div 5{,}343{,}297 = 0.088 = 8.8$ per cent. of the total heat received by the stoves, leaving 91.2 per cent. to be applied to heating the blast and for radiation and conduction loss. The last two items, however, must amount to 1,701,998 Calories, and, therefore, the total heat requirement of the stoves is

$$\frac{1{,}701{,}998}{0.912} = 1{,}866{,}200 \text{ pound Calories,}$$

requiring

$$\frac{1{,}866{,}200}{5{,}343{,}297} = 0.349 = 34.9 \text{ per cent.} \qquad (2)$$

of all the gas produced by the furnace.

In the above solution the only uncertain factor in the calculation is the radiation and conduction loss from the stoves, and this uncertainty does not largely affect the reliability of the result obtained, allowing that we have assumed an approximately correct value for this loss. All uncertainty could be dispelled, however, were the radiation and conduction losses measured directly. This could be accomplished by finding experimentally the temperature of the outside shells of the stoves, and calculating the external losses of heat by the laws of radiation and conduction; but in order to do this satisfactorily, it would be necessary to divide the shells of the stoves into zones, and determine the temperature and calculate the losses from each zone separately—a rather long operation, but one worth doing.

Drying Air Blast.

The advantage of dried blast has been already discussed at length in these calculations. The advantage is due primarily to the higher temperature obtained when the moisture has been removed.

The means adopted commercially for drying the air have

been those of refrigerating the uncompressed air, before its entrance into the blowing cylinders. This has the great advantage of furnishing the cylinders with cold air, and, therefore, of greatly increasing their blowing capacity, since the weight or quantity of air blown is proportional to the absolute temperature of the air entering the cylinders.

Illustration. Outside air being at 30° C., what increase in the amount of air furnished by blowing engines will result if the temperature of the air is artificially reduced to −5° C.? How much slower can the engines be driven, in the second case, in order to furnish the same weight of air as before?

The two temperatures are respectively 273+30 and 273−5 absolute, that is, 303 and 268. The engines, if run at uniform speed, would furnish 303÷268 = 1.13 times as much air in the second case, or 13 per cent. more. If the engines were slowed down to 268÷303 = 0.884 of their former speed they would furnish the same amount of air; that is, they could be run 11.6 per cent. slower. In fact, they could be run more than 11.6 per cent. slower in the second case, and yet supply the same quantity of air, because at the slower running the delivery efficiency is somewhat higher.

The disadvantage of cooling the uncompressed blast is that it must be cooled much more, to eliminate from it a given percentage of its moisture, than if it were first compressed, and to obtain nearly dry air the moisture must be practically frozen out.

Illustration: Air at 30° C. and 85 per cent. humidity is to be cooled until 95 per cent. of its moisture is eliminated, without compression; to what temperature must it be cooled?

From the tables of aqueous tension, we find that the maximum tension which aqueous vapor can exert at 30° C. is 31.5 millimeters, which means practically that $\frac{31.5}{760}$ of a cubic meter of moisture accompanies $\frac{728.5}{760}$ of a cubic meter of air proper. If the humidity is 85 per cent., then this same quantity of air is accompanied by

$$\frac{31.5}{760} \times 0.85 = 0.0352 \text{ cubic meters}$$

of moisture, or, per cubic meter of air measured dry—

$$0.0352 \div \frac{728.5}{760} = 0.0368 \text{ cubic meters.}$$

If 95 per cent. of this is removed by cooling, then the moisture left, per cubic meter of air measured dry, is

$$0.0368 \times 0.05 = 0.00184 \text{ cubic meters.}$$

And the relative tensions of air and moisture, to attain this dryness, must have been reduced to

$$1.0000 : 0.00184.$$

Since the sum of these tensions is always 760 mm. in the uncompressed air, the actual tensions of air and moisture will be

$$758.6 : 1.4,$$

that is, the temperature must be reduced until the moisture present can exert only 1.4 mm. pressure. This, on examining the tables of tension of aqueous vapor is found to be less than 0° C., in fact −15° C.

Problem 62.

Air at 30° C., carrying 85 per cent. of its possible amount of moisture, is cooled to 0° C., and the moisture condensed to liquid water at that temperature. Barometer 760 mm.

Required:

(1) The percentage of the moisture condensed.

(2) The amount of heat to be abstracted from each cubic meter of original moist air (refrigerating effect).

(3) The percentage of moisture which would be condensed if the temperature were reduced to −5° C.

(4) The total heat to be abstracted, per cubic meter of original air, in the latter case.

Solution:

(1) From the preceding illustration we can take the figures that in the moist air taken, each cubic meter of air proper is accompanied by 0.0368 cubic meter of moisture. In the cooled

air at 0°, the relative volumes of air proper and residual moisture will be as their relative tensions, viz.:

$$755.4:4.6$$

or

$$1:0.0061.$$

The moisture accompanying the given quantity of air is, therefore, reduced from 0.0368 to 0.0061, showing a condensation of 0.0307, equal to

$$\frac{0.0307}{0.0368} = 0.834 = 83.4 \text{ per cent.} \qquad (1)$$

(2) The air at 30° contains, as before figured out, air proper and moisture in the proportions

$$1:0.0368.$$

or, in 1 cubic meter of moist air, in the proportions

$$0.9645:0.0355.$$

We have, therefore, to calculate the heat to be extracted from 0.9645 cubic meter of air proper, falling 30° to 0°, and from 0.0355 cubic meter of water vapor, falling 30° to 0° and 83.4 per cent. of the latter condensing to liquid at 0°. The figures are, remembering that the volumes heretofore handled are at 30°:

Air proper:

$$0.9645 \times \frac{273}{303} \times 0.3038 \times 30 = 7.920 \text{ Calories}$$

Moisture, if all uncondensed:

$$0.0355 \times \frac{273}{303} \times 0.3445 \times 30 = 0.332 \text{ "}$$

Heat of condensation:

$$0.0355 \times 0.834 \times \frac{273}{303} \times 0.81 \times 606.5 = 13.105 \text{ "}$$

$$\text{Total} = 21.357 \text{ "} \qquad (2)$$

(3) If the temperature were reduced to −5° C., the tension of the residual moisture would be 3.4 mm. of mercury, and

that of the air proper 756.6 mm., their relative volumes would be in the same ratio, viz.:

$$756.6:3.4$$

or

$$1:0.0045.$$

showing that out of 0.0368 cubic meter of moisture originally accompanying 1 cubic meter of air proper, 0.0323 had been condensed, or

$$\frac{0.0323}{0.0368} = 0.878 = 87.8 \text{ per cent.} \qquad (3)$$

(4) The condensation is seen to be 87.8−83.4, or 4.4 per cent. more, if the air is cooled to −5° C. A considerably larger amount of refrigeration, however, is required in this case, because the moisture would all be frozen. The 1 cubic meter of moist air at 30°, containing, as before calculated, 0.9645 cubic meter of air proper and 0.0355 cubic meter of moisture, would have 87.8 per cent. of the latter condensed to ice, or 0.03117 cubic meter, and, therefore, 0.00433 cubic meter remaining uncondensed.

Air proper, 30° to −5° C.:

$$0.9645 \times \frac{273}{303} \times 0.3037 \times 35 = 9.237 \text{ Calories}$$

Moisture, if all uncondensed, 30° to −5° C.:

$$0.0355 \times \frac{273}{303} \times 0.3438 \times 35 = 0.385 \text{ "}$$

Condensation of 0.03177 m^3 to liq. at − 5° C.:

$$0.03177 \times \frac{273}{303} \times 0.81 \times 605 = 14.025 \text{ "}$$

Freezing of same, at − 5° C.:

$$0.03177 \times \frac{273}{303} \times 0.81 \times 80 = 1.855 \text{ "}$$

$$= 25.502 \text{ "} \qquad (4)$$

The conclusion is, that an increased condensation of 4.4 per cent. has been obtained by an increase in the refrigerating requirement of 25.502−21.357 = 4.145 Calories, or nearly

20 per cent. Another way of stating the comparison, is that when not freezing the moisture condensed, about 4 per cent. of the moisture was condensed from each cubic meter of air for one Calorie of refrigeration, whereas, the removal of additional moisture by cooling below zero requires nearly one Calorie refrigeration for each additional per cent. of moisture eliminated.

A practical conclusion is, that the expense of refrigeration might easily be justified down to 0° C., and yet be unjustified by the results when cooling below 0°.

Mr. James Gayley has, I believe, patented the scheme of refrigerating the air in two stages; first, nearly to zero, removing the moisture thus condensed as liquid, and then cooling the nearly dry air further, eliminating more moisture as ice. In this manner, the amount of refrigeration required is reduced by the latent heat of solidification of the larger part of the moisture, and cooling below zero becomes profitable. The saving in the above example would be 80 Calories per kilogram on all the moisture condensed at 0°, viz.:

$$0.0216 \times 80 = 1.728 \text{ Calories},$$

cutting down the refrigeration required from 25.502 to 23.774 Calories, that is, enabling 4.4 per cent. additional drying to be produced for 2.4 Calories additional refrigeration. This scheme of Mr. Gayley is founded on sound scientific as well as practical considerations.

The idea of cooling the compressed blast by moderately cool water, recently proposed, is also a very practical idea and founded on sound scientific principles. At a given temperature moisture cannot exert more than a maximum vapor tension. It follows that if we start with air saturated with moisture, at a given temperature, and compress it to double its initial tension, keeping its temperature constant, about half of its moisture must condense out. If, at the same time, it is artificially cooled, then more than half of its moisture will condense as liquid.

If we start with air not saturated with moisture, the compression, temperature being constant, will increase the tension of the moisture present until the air becomes saturated, after which increased pressure will cause condensation.

Illustration: Air at 30° C., 85 per cent. saturated with moisture, is compressed. At what effective pressure does it become saturated with moisture, temperature remaining constant?

The moisture present is exerting 85 per cent. of its maximum vapor tension at this temperature. Therefore, the tension must be increased in the ratio of 85 to 100, to make the air saturated, viz.: in the ratio 1 to 1.177. The effective pressure necessary to be applied is, therefore, $1.177 - 1.000 = 0.177$ atmospheres (2.6 pounds per square inch).

Illustration: If air at 30° C., 85 per cent. saturated with moisture, is compressed to one atmosphere effective pressure and its temperature kept constant, what proportion of its moisture will condense?

Before compression, the tension of the moisture being $31.5 \times 0.85 = 26.8$ mm., the relative volumes of air proper and moisture are as

$$733.2 : 26.8$$

or, as

$$1 : 0.0367$$

After compression, the tension on the mixture being two atmospheres (1520 mm.), and the tension of the uncondensed moisture being it maximum, or 31.5 mm., the relative volumes of air and uncondensed moisture will be as

$$1488.5 : 31.5,$$

or, as

$$1 : 0.0212.$$

The proportion of the original moisture remaining uncondensed is therefore,

$$\frac{0.0212}{0.0367} = 0.578 = 57.8 \text{ per cent.}$$

and the amount condensed out = 42.2 per cent.

Problem 63.

Air at 30° C., and 85 per cent. saturated with moisture is compressed to one atmosphere effective pressure (760 mm. of mercury), and simultaneously cooled by river water to 10° C. Barometer 730 mm.

Required:

(1) The percentage of the original moisture, condensed.

(2) The weight of moisture remaining in the air, expressed in grams per cubic meter of dry air at standard conditions (*i.e.*, per 1.293 kilograms of air proper).

Solution: (1)

Tension of uncompressed moist air	=	730.0 mm.
Tension of moisture present 31.5×0.85	=	26.8 "
Tension of air proper, uncompressed	=	703.2 "
Relative volumes of air proper and moisture	=	1 : 0.0381
Tension of compressed moist air $730+760$	=	1490.0 "
Tension of uncondensed moisture (maximum tension at 10°)	=	9.1 "
Tension of air proper, when compressed	=	1480.9 "
Relative volumes of air proper and uncondensed moisture	=	1 : 0.0061

Proportion of moisture condensed:

$$\frac{0.0381 - 0.0061}{0.0381} = 0.84 = \mathbf{8.40} \text{ per cent.} \qquad (1)$$

(2) The relative volumes of air proper and uncondensed moisture are, as found above,

$$1 : 0.0061,$$

And the relative specific gravities of air proper and moisture are as the standard weights of 1 cubic meter of each, viz.: as

$$1.293 : 0.81.$$

It follows, therefore, that 1.293 kilos. of air proper (1 cubic meter at standard conditions) must be accompanied by

$$0.0061 \times 0.81 = 0.0049 \text{ kg. of moisture,}$$

or $$= \mathbf{4.9} \text{ grams.} \qquad (2)$$

The original moist air contained, similarly considered,

$$0.0381 \times 0.81 = 0.0309 \text{ kg.}$$
$$= 30.9 \text{ grams.}$$

CHAPTER VII.

THE BESSEMER PROCESS.

The outlines of this famous process are known to every educated person; the mechanical and most of the chemical details are familiar to most technologists; the exact way to run the converter is the source of income to hundreds of superintendents of works, and yet the quantitative side of the chemical and physical operations involved is mastered by very few.

To state the case briefly, melted pig iron is put into the converter, numerous air jets are blown through, the impurities of the iron—carbon, silicon, manganese and, in a special case, phosphorus—oxidize relatively faster than the iron, and the final product is usually nearly pure iron. This is recarburized to steel by spiegel-eisen. During the blow very little free oxygen escapes from the converter, and the gases produced are principally nitrogen, carbon monoxide and some carbon dioxide, while some hydrogen may come from the decomposition of the moisture of the air. The silicon, manganese, phosphorus and iron form silica, manganous oxide (MnO) principally, ferrous oxide (FeO) principally, phosphorus pentoxide, P^2O^5, which go into the slag, while a little Fe^2O^3, Mn^3O^4 and SiO^2 escape as fume.

The applications of calculations to this process are numerous and important. They include such subjects as the amount of air theoretically required per ton of iron, the dimensions and power of the blowing engines, the weight of slag produced, the balance sheet of materials, the balance sheet of heat evolved and distributed, the radiation losses, the discussion of the efficiency of the various impurities as heating agents in the process.

Air Required.

Basing our calculations on the analysis of the pig iron used, and assuming it to be blown to pure iron, we must next assume the probable loss of iron itself in the blow. This varies

considerably, from 1 to 10 per cent, on the pig iron used in ordinary practice, but as much as 20 to 25 per cent. in some carelessly run "Baby" Bessemers in steel-casting foundries. The silicon all oxidizes to SiO^2; iron mostly to FeO, and a small part, say not over one-tenth, to Fe^2O^3; manganese mostly to MnO, a small part, up to one-fourth, may form Mn^2O^3; phosphorus forms only P^2O^5; carbon burns mostly to CO, but from one-fifth, at times nearly one-half, burns to CO^2. When all the calculated oxygen has been found, the blast to contain it can be calculated, if it is assumed that no free oxygen escapes from the converter; at times, however, up to one-third of all the oxygen blown in may thus escape, but this is very exceptional, ordinarily less than one-fifth thus escapes, and often none at all.

Problem 64.

Pig iron containing 3.10 per cent. carbon, 0.98 silicon, 0.40 manganese, 0.101 phosphorus and 0.06 sulphur is blown in an acid-lined converter, to metal practically free from carbon, silicon and manganese, but no sulphur or phosphorus is eliminated. To get the minimum and the maximum amounts of air which could be needed, make the following assumptions:

	Case 1.	*Case* 2.
Per cent. of iron lost by oxidation.....	1	15
Proportion of iron oxidized to Fe^2O^3.....	none	one-tenth
Proportion of Mn oxidized to Mn^2O^3.....	none	one-fifth
Proportion of C oxidized to CO^2.....	one-fifth	one-half
Proportion of O^2 escaping in the gases.....	none	one-third

Requirement: (1) Find the weight of dry air needed per metric ton of pig iron blown, in each case, and its volume at 0° C. Express the results also in pounds and cubic feet per ton of 2,000 pounds.

Solution:

Case 1.

Oxygen needed per 1,000 kg. of pig iron:

C to CO^2..... 6.2 kg. $\times \frac{32}{12}$ = 16.53 kg.

C to CO.....24.8 " $\times \frac{16}{12}$ = 33.07 "

Si to SiO^2 ..... 9.8 " $\times\frac{32}{28}$ = 11.20 kg.

Mn to MnO ..... 4.0 " $\times\frac{16}{55}$ = 1.16 "

Fe to FeO ..... 10.0 " $\times\frac{16}{56}$ = 2.86 "

64.82 "

N^2 accompanying = 216.07 "

Air needed ..... = 280.89 "
Volume at 0° C ..... = 217.2 m^3
Volume needed per 1000 oz. Av ..... = 217.2 ft^3
Volume needed per 2000 lbs. Av ..... = 6,950 ft^3

Case 2.

Oxygen needed per 1000 kg. of pig iron:

C to CO^2 ..... 15.5 kg. $\times\frac{32}{12}$ = 41.33 kg.

C to CO ..... 15.5 " $\times\frac{16}{12}$ = 20.67 "

Si to SiO^2 ..... 9.8 " $\times\frac{32}{28}$ = 11.20 "

Mn to MnO ..... 3.2 " $\times\frac{16}{55}$ = 0.93 "

Mn to Mn^2O^3 ..... 0.8 " $\times\frac{48}{110}$ = 0.34 "

Fe to FeO ..... 135.0 " $\times\frac{16}{56}$ = 38.57 "

Fe to Fe^2O^3 ..... 15.0 " $\times\frac{48}{112}$ = 6.43 "

O^2 unused (one-half sum of above) ..... = 59.73 "

179.20 "

N^2 accompanying = 597.33 "

Air used ..... = 776.53 "
Volume at 0° C ..... = 600 m^3
Volume used per 1000 oz. Av ..... = 600 ft^3
Volume used per 2000 lbs. Av ..... = 19,200 ft^3

For temperatures of the air above 0° C., a corresponding increase in the volume used would be found. Since this is net air received by the converter an allowance for loss of 10 to 25 per cent. (in exceptional cases 50 per cent.) would be needed to get the piston displacement of the blowing engines. The above figures are the maximum and minimum for this quality of pig iron only, blown in an acid-lined converter; other qualities of pig iron might require a little more or less, and if blown in a basic-lined converter considerably more, to oxidize the phosphorus. The detailed calculations can be made in each specific case.

Air Received.

The converse of the preceding proposition is to take an actual case, in a Bessemer converter, and to calculate how much air is being received. This will serve as a check on the blowing engines, since the volume received, divided by the piston displacement, gives the volume efficiency of the blowing plant. To make the calculation we need to know the weight and analysis of the pig iron and the analysis of the blown metal, in order to find the weights of impurities oxidized, also the average composition of the escaping gases, to find the proportion of carbon burning to CO^2 and of unused oxygen; also the composition of the slag, to get therefrom the weight of iron oxidized and the weight of slag, if practicable, but this can sometimes be calculated; also the weight and composition of the fume, if it is considerable. The temperature of the air entering the blowing cylinders its hygrometric condition and the barometric pressure should also be noted.

Problem 65.

At the South Chicago works of the Illinois Steel Co. (see paper by Howe, in Trans. American Institute of Mining Engineers, XIX. [1890–91], p. 1127), the charge weighed 22,500 pounds, and contained 2.98 per cent. carbon, 0.94 silicon, 0.43 manganese, 0.10 phosphorus, and 0.06 sulphur. After blowing 9 minutes 10 seconds the bath contained 0.04 per cent. carbon, 0.02 silicon, 0.01 manganese, 0.11 phosphorus and 0.06 sulphur. The slag formed contained 63.56 per cent. silica, 3.01 alumina, 21.39 FeO, 2.63 Fe^2O^3, 8.88 MnO, 0.90 CaO and 0.36 MgO, of

which the Al^2O^3, Cal and MgO and part of the SiO^2 come from the lining. The gases, analyzed dry, show an average composition during the blow of

CO^2	5.20 per cent.
CO	19.91 "
H^2	1.39 "
N^2	73.50 "

and were free from fume.

The piston displacement during the blow was 190,406 cubic feet, air in engine room 36° C., humidity 50 per cent., barometer 756 millimeters.

Requirements: (1) The weight of oxygen acting on the bath during the blow, and the theoretical volume of air at standard conditions to which this would correspond, per 2,000 pounds of metal blown.

(2) The volume of moist air at the conditions of the engine room, received by the converter during the blow, and the volume efficiency of the blowing machine and connections.

(3) The weight of slag produced and the loss in weight of the lining by corrosion during the blow.

Solution: (1) The percentages of impurities left in the bath are so small that we can take them as equivalent to the same percentages reckoned on the original weight of the bath If they had been larger it would be necessary to assume an approximate loss of iron during the blow, find the final weight of the bath and reckon the percentages on this revised weight.

Making this assumption, we know at once the weights of carbon, silicon and manganese oxidized, but we do not know the weight of iron lost. That follows, however, from a consideration of the slag, for the manganese and iron in the slag are derived only from the metallic bath, and the analysis of the slag practically gives us the relation between the weights of manganese and iron in it; since we know the weight of the former oxidized, the weight of iron lost can be calculated. Thus the slag contains:

MnO	8.88 per cent	=	6.88 per cent.	Mn	
FeO	21.39 "	=	16.64 "	Fe as FeO	
Fe^2O^3	2.63 "	=	1.84 "	Fe as Fe^2O^3	

The loss of manganese being 0.42 per cent. = 94.5 pounds, the loss of iron is:

$$94.5 \times \frac{16.64}{6.88} = 228.6 \text{ pounds Fe as FeO}$$

$$94.5 \times \frac{1.84}{6.88} = 25.3 \text{ pounds Fe as } Fe^2O^3$$

The remaining item still undetermined is the weight of carbon oxidizing to CO^2 and to CO. The gas analysis shows 5.20 per cent. CO^2 to 19.91 per cent. CO, and since equal volumes of each of these gases contain equal weights of carbon, it follows that $\frac{5.20}{25.11}$ of the total carbon is present in the gas as CO^2, and the rest as CO. Since the total carbon oxidized is $22{,}500 \times 0.0294 = 661.5$ pounds, we have

$$661.5 \times \frac{520}{2511} = 137.0 \text{ pounds C burning to } CO^2$$

$$= 524.5 \quad " \quad " \quad CO$$

Weight of oxygen absorbed by the bath:

C to CO^2	137.0 pounds	× 8/3	= 365.3	pounds
C to CO	524.5 "	× 4/3	= 699.3	"
Si to SiO^2	207.0 "	× 32/28	= 236.6	"
Mn to MnO	94.5 "	× 16/55	= 27.5	"
Fe to FeO	228.6 "	× 16/56	= 65.3	"
Fe to Fe^2O^3	25.3 "	× 48/112	= 10.8	"
			1404.8	"
N^2 corresponding			= 4682.7	"
Dry air corresponding			= 6087.5	"
Volume at 0° C			= 75,483	ft^3
Weight of O^2 per 2000 pounds			= 124.9	lbs. (1)
Volume of air per 2000 pounds			= 6,710	ft^3 (1)

(This result is for comparison with data of Problem 64).

(2) The nitrogen in the gases can be obtained from its volume relation to the carbon, and from this we can calculate the real volume of blast used.

Weight of carbon in 1 cubic foot of gases:

$$(0.0520+0.1991)\times 0.54 = 0.1356 \text{ oz. Av.}$$

Volume of gases produced at standard conditions:

$$\frac{661.5\times 16}{0.1356} = 78{,}057 \text{ ft}^3$$

Volume of nitrogen at standard conditions:

$$78{,}057\times 0.7350 = 57{,}372 \text{ ft}^3$$

$$\text{Weight} = 57{,}372\times 1.26 = 72{,}289 \text{ oz. Av.}$$

$$= 4{,}518 \text{ lbs.}$$

The question now is, how much nitrogen is contained in each cubic foot of air in the engine room. Knowing that, we are prepared to calculate the volume of this actually received by the converter:

Barometric pressure	=	756 m.m.
Tension of moisture (44×0.5)	=	22 "
Tension of air present	=	734 "
Tension of nitrogen present (734×0.792)	=	580 "

Weight of nitrogen in 1 cubic foot:

$$1.26\times\frac{273}{273+36}\times\frac{580}{760} = 0.8495 \text{ oz. Av}$$

Volume of air actually received:

$$\frac{4{,}518\times 16}{0.8495} = 85{,}095 \text{ ft.}^3 \qquad (2)$$

Volume efficiency of machinery:

$$\frac{85{,}095}{190{,}406} = 0.447 = 44.7 \text{ p. c. (2)}$$

(3) The slag contains 8.88 per cent. of MnO, equal to 6.88 per cent. of Mn, as already calculated. But 94.5 pounds of

manganese is oxidized, therefore, the weight of slag produced is:

$$94.5 \div 0.0688 = 1374 \text{ pounds.} \qquad (3)$$

Weight of SiO^2 in slag (1374×0.6356)	= 873	pounds
SiO^2 from the Si of bath ($207.0 + 236.6$)	= 444	"
SiO^2 corroded from the lining	= 429	"
CaO, Al^2O^3 and MgO (1374×0.0427)	= 59	"
Loss in weight of lining	= 488	" (3)

Blast Pressure.

It is necessary to use sufficient blast pressure to overcome the static pressure of the metallic bath, plus that of the slag formed, also the back pressure in the converter, to give the necessary velocity to the air in the tuyeres and to overcome friction in the same. When the tuyeres are near to the surface of the bath, pressures of 1 or 2 pounds will run the small converter, but the ordinary converter with bottom tuyeres requires from 15 to 30 pounds pressure per square inch (1.054 to 2.108 kg. per square c.m.). We will consider the latter, the more frequent and the more complex case to discuss.

The metal lies 12 to 24 inches (30 to 60 c.m.) deep in the converter. Since its specific gravity melted is about 6.88 (Roberts and Wrightson), the ferro-static pressure which it exerts is practically 0.25 pounds per square inch for each inch depth of metal, or 0.00688 kilos. per square centimeter for each centimeter depth.

The slag lying on the metal has a specific gravity melted of approximately half that of the metal. Its amount may vary from 5 to 10 per cent. of the weight of the metal treated, in an acid-lined converter, up to from 15 to 35 per cent. in a basic-lined vessel. Taking into account its lower specific gravity, its depth in the converter may be, therefore 10 to 20 per cent. the depth of metal in an acid-lined vessel, and 30 to 70 per cent. in a basic-lined converter; but the static pressure exerted would be only in direct proportion to the relative weights; *i. e.*, 5 to 10 or 15 to 35 per cent. of that exerted by the metal. The static pressure of the slag may, therefore, be reckoned as 0.125 pounds per square inch for each inch in depth, or 0.00344

kilos. per square centimeter for each centimeter depth, and the depth of slag as lying between the following extremes:

		Acid Lined.	*Basic Lined.*
Depth of metal	Inches.....	12 to 24	12 to 24
	Centimeters..	30 to 60	30 to 60
Depth of slag	Inches.....	1.2 to 4.8	3.6 to 16.8
	Centimeters..	3.0 to 12.0	9.0 to 42.0

The probable depth of slag can be calculated in any particular case, when the composition of the metal to be blown is known, its approximate depth in the vessel, and the approximate composition of the slag to be formed.

The back pressure of gases in the converter itself, that is, their static pressure, will vary with the shape of the converter and the size of the free opening for their escape into the air. A measurement at the Pennsylvania Steel Co's. works gave 0.275 pounds per square inch, but it is not stated just how the measurement was made. If we know approximately the volume of gas which must escape from the converter and from its temperature and the time and the size of the outlet calculate its velocity, the static pressure giving it this velocity can be calculated as

$$h = \frac{V^2}{2g}$$

in which, if V is in feet per second, $2g = 64.3$ and the resultant pressure is in feet of the hot gas; if V is in meters per second, $2g = 19.6$, and h is in meters of the hot gas. Knowing the approximate specific gravity of the hot gas (weight of 1 cubic foot in pounds or of 1 cubic meter in kilograms) the static pressure is obtainable in pounds per square foot or kilograms per square meter.

Illustration: The gases escaping from a converter are 78,057 cubic feet (standard conditions), and weigh 0.0801 pounds per cubic foot (standard conditions). They escape from the converter at an average temperature of 1,500° C., and the opening is 24 inches in diameter. What is the gaseous back pressure in the converter? Time of blow 9 minutes 10 seconds.

Volume of gas at 1,500°:

$$78{,}057 \times \frac{1500+273}{273} = 506{,}940 \text{ ft}^3$$

Volume per second:

$506{,}940 \div 550 = 921.7$ "

Area of outlet:

$2 \times 2 \times 0.7854 = 3.1416$ ft²

Velocity (assuming 0.9 coefficient):

$921.7 \div 0.9 \div 3.1416 = 326$ ft. per second

Head of hot gas giving velocity:

$$h = \frac{326 \times 326}{64.3} = 1{,}653 \text{ ft.}$$

Pressure of this column per square foot:

$$1.653 \times \frac{273}{1773} \times 0.0801 = 20.4 \text{ pounds}$$

Per square inch = 0.14 "

This solution omits one consideration; the velocity of the gases in the body of the converter is neglected. This is somewhat counterbalanced by the great friction of the gases against the sides of the converter, so that the one item tends to neutralize the other. If the interior were 8 feet in diameter, the velocity of the gases therein would average only some 20 feet per second, showing the above corrections to be practically negligible, since the pressure thus represented would be only 0.4 per cent. of the total obtained above.

The pressure necessary to force the blast through the tuyeres is calculable on principles similar to the above; the differences are that the blast, at temperatures varying from 100° C. in the blast box to possibly 200° at its entrance into the metal, is divided up into fifty or 150 streams of approximately 1 centimeter (0.4 inch) in diameter, the length of tuyeres being some 50 centimeters (20 inches). The formula similar to that used

for chimney draft, or rather, frictional resistance in a chimney, applies to this case.

$$h = \frac{V^2}{2g} \frac{KL}{D}$$

in which h is the head in terms of the air passing, V is its velocity, 2g the gravitation constant, L the length of the tuyere, D its diameter, and K the coefficient of friction, which latter is for relatively smooth flues 0.05 (Grashof), and may be so assumed here.

Problem 66.

In the converter mentioned in Problem 65, where 22,500 pounds of metal was blown in 9 minutes 10 seconds, using as therein calculated 85,095 cubic feet of air, at 36° C., and producing 1,374 pounds of slag, assume the inside diameter of the converter as 7 feet, and that the bottom contains fourteen tuyere blocks, each containing eleven openings of 0.5 inch diameter each; blocks 24 inches long. Assume back pressure in converter 0.14 pounds per square inch, total blast pressure in equalizing reservoir 27 pounds per square inch. Temperature of air in the tuyeres 150° C.

Required: (1) The pressure needed to overcome the head of metal and slag.

(2) The pressure absorbed in friction in the tuyeres.

(3) The pressure represented by the velocity of the blast in the tuyeres.

(4) The loss of pressure from the reservoir to the blast-box.

(5) The distribution of the total pressure.

(6) The length of the blow if the blast pressure were reduced to 20 pounds.

(7) The length of the blow if the pressure were maintained at 27 pounds, but twenty-one tuyere blocks (each with eleven ½-inch holes) were used.

Solution: (1) At the start there is 22,500 pounds of melted metal, the volume of which will be

$$\frac{22{,}500}{6.88 \times 62.5} = \frac{22{,}500}{430} = 52.3 \text{ cubic feet}$$

The depth of metal, the inside diameter being 7 feet, is

$$\frac{52.3}{7\times7\times0.7854} = \frac{52.3}{38.5} = 1.356 \text{ feet}$$

$$= 16.4 \text{ inches}$$

Static pressure $= 16.4\times 0.25 = 4.1$ lbs. per sq. in.

The slag, formed during the first half of the blow, weighs 1,374 pounds, and has a volume of

$$\frac{1374}{3.44\times62.5} = \frac{1374}{215} = 6.4 \text{ cubic feet}$$

The depth of slag, at its maximum, will be

$$6.4\div38.5 = 0.167 \text{ feet}$$

$$= 2.0 \text{ inches}$$

Static pressure $2.0\times0.125 = 0.25$ lbs. per sq. in.

The static pressure during the blow will, therefore, be 4.1 pounds to start with, increasing during the first half of the blow to 4.35 pounds, and staying practically constant at that, and, therefore, will average

$$\frac{4.1+4.35}{2\times2}+\frac{4.35}{2} = 4.29 \text{ pounds} \qquad (1)$$

(2) Each of the $14\times11 = 154$ tuyeres receives $85{,}095\div154\div550 = 1.005$ cubic feet of air per second, measured at 36° C. At 150° C. this volume is

$$1.005\times\frac{273+150}{273+36} = 1.375 \text{ cubic feet}$$

And the velocity in the tuyere:

$$1.375\div\frac{0.5\times0.5\times0.7854}{144} = 1009 \text{ feet per second}$$

The head absorbed in friction in the 24-inch tuyeres will be

$$h = \frac{1009\times1009}{64.3}\times\frac{0.05\times2}{0.0417} = 37{,}893 \text{ feet}$$

Changing this pressure of air at 150° C. to pounds per square inch we have:

Weight of 1 cubic foot of air at 0° = 0.0808 pounds
Weight of 1 cubic foot of air at 150° = 0.0522 "
Weight of air column = 37,893×0.0522 = 1978 "
Pressure in pounds per square inch = **13.7** " (2)

(3) The pressure absorbed as velocity has already been expressed in getting the friction in the tuyeres. The velocity head is simply:

$$h = \frac{V^2}{2g} = \frac{1009 \times 1009}{64.3} = 15{,}835 \text{ feet}$$

which becomes in pressure

15,835×0.0522 = 826.6 pounds per square foot
= **5.73** pounds per square inch (3)

(4) The remaining part of the 27 pounds pressure used is lost between the blast reservoir and the entrance to the tuyeres. It is

27.00 − (13.70 + 5.73 + 4.29 + 0.14). = **3.14** pounds. (4)

(5) Distribution of blast pressure:

Fall between reservoir and tuyeres	= 3.14 pounds	=	11.6%
Absorbed in friction in the tuyeres	= 13.70 "	=	50.7%
Absorbed in velocity in the tuyeres	= 5.73 "	=	21.2%
Static head of liquid bath	= 4.29 "		15.9%
Velocity head of issuing gases	= 0.14 "	=	0.6%
	27.00 "	=	100.0%

(6) All the items of absorption of pressure are proportional to the square of the velocity of the gases, excepting the static pressure of the bath. It remains constant at 4.29 pounds. If the total pressure were reduced to 20 pounds, there would be only 20 − 4.29 = 15.71 pounds pressure to give velocity and overcome friction, instead of 27 − 4.29 = 22.71 pounds. The relative quantities of air blown through in a given time in the two instances would be practically proportional to the square roots of the two effective pressures, *i.e.*:

$$\sqrt{22.71} : \sqrt{15.71} = 1 : 0.832$$

and the times of the blows inversely as the latter:

550 sec. ÷ 0.832 = 673 seconds
= **11 min. 13 sec.** (6)

(7) If the tuyere area were increased 50 per cent., then the velocity of the air in the tuyeres would be decreased one-third, assuming the amount of air passing to be unchanged. This would decrease the pressure absorbed in friction, and in giving velocity in the tuyeres to $(0.67)^2 = 0.444$ of its former amount. The 19.43 pounds previously absorbed in these two items would then become $19.43 \times 0.444 = 8.61$ pounds, and the total pressure needed to run the converter just as fast as before would be $27 - (19.43 - 8.61) = 16.18$ pounds per square inch. If, however, the pressure were maintained at 27 pounds, giving still $27 - 4.29 = 22.71$ pounds to overcome frictional resistances and to give velocity, then the velocity and consequent amount of air blown through by this 22.71 pounds pressure would increase in proportion to the square root of these two available pressures; *i.e.*, be as

$$\sqrt{16.18 - 4.29} : \sqrt{27 - 4.29} = 1 : 1.38$$

The duration of the blow would be just that much shorter; *i.e.*:

$$550 \text{ sec.} \div 1.38 = 398 \text{ seconds}$$
$$= \textbf{6 min. 38 sec.} \qquad (7)$$

Flux and Slag.

No flux is used in the acid-lined converter, and the silica, iron oxides and manganese oxide formed in the converter unite to a silicate slag which corrodes the lining and thus takes up more silica. The slag being analyzed, its weight is obtained by considering the percentage of manganese which it contains, because the weight of manganese oxidized is known definitely from the analysis of the bath; it is usually all oxidized. Calculation of the weight of slag cannot be based upon the silica, because an unknown amount comes from the lining; nor upon the iron, because the weight of iron left in the converter is not definitely known. Having the weight of the slag, analysis tells us the total weight of silica in it, as also the amount of iron. The silica in the slag minus that formed from silicon in the pig iron, gives silica corroded from the lining.

In the basic Bessemer converter, phosphorus is nearly entirely eliminated from the metal, so that, assuming none to be volatilized, the amount going into the slag is known, and using the slag analysis the weight of slag can be calculated. In

this process the lining is mainly dolomite, containing CaO and MgO, in proportion easily determined by analysis. The weight of slag being known, the amount of corrosion of the lining can be determined from the percentage of magnesia therein, which may be assumed as practically coming entirely from the lining; it cannot be told from the CaO in the slag, because nearly pure CaO is added during the blow, and some of it, a variable amount, gets blown out of the converter. For the same reason it is not possible to base a good calculation of the weight of slag on the lime alone which is added, because of the indefinite proportion of it which is blown out. The weight of slag may also be gotten from the silica or manganese oxide in it, assuming these to come almost entirely from the oxidation of silicon or manganese.

Lime must be added as flux, in the basic converter, to protect the lining and to make the slag so basic that the percentage of silica in it is below 15 per cent., phosphoric acid below 20 per cent., and lime over 50 per cent. These considerations must be balanced in each particular case.

Illustration: Pig iron blown in a basic-lined converter contained 1.22 per cent. silicon, 2.18 phosphorus, 1.03 manganese and 3.21 carbon. It is blown until all of these and 2.00 per cent. of iron are oxidized, and burnt lime is added to form slag during the blow. Composition of the burnt lime: MgO, 1.00 per cent.; SiO^2, 2.00 per cent.; CaO, 97 per cent. How much lime should be added per 10 metric tons of pig iron charged?

The slag-forming ingredients from the oxidation of the bath, and the addition of X kilos. of lime, are

SiO^2	$10{,}000 \times 0.0122 \times 60/28$	$= 261.4$ kg.
P^2O^5	$10{,}000 \times 0.0218 \times 142/62$	$= 499.3$ "
MnO	$10{,}000 \times 0.0103 \times 71/55$	$= 133.0$ "
FeO	$10{,}000 \times 0.0200 \times 72/56$	$= 257.1$ "
CaO	$X \times 0.9700$	$= 0.97\ X$
MgO	$X \times 0.0100$	$= 0.01\ X$
SiO^2	$X \times 0.0200$	$= 0.02\ X$

Weight for slag $= X + 1150.8$ kg.

Corrosion of the lining will undoubtedly increase this weight, so some allowance should be made, say to increase it 5 per

cent., probably an outside figure. Of this 5 per cent., half can be considered lime and half magnesia. The total weight of slag will then be 1.05 X+1208.3, and of the ingredients principally in question:

SiO^2 = 261. kg. +0.02 X
MgO = 28.7 " +0.035 X
CaO = 28.7 " +0.995 X

To make our slag 50 per cent. CaO will require the addition of enough to make

$$28.7+0.995\ X = 0.50\ (1.05\ X+1208.3)$$
$$X = \mathbf{1224}\text{ kg.}$$

To make a slag with at most 15 per cent. of SiO^2 requires

$$261.4+0.02\ X = 0.15\ (1.05\ X+1208.3)$$
$$X = \mathbf{583}\text{ kg.}$$

To make a slag with at most 20 per cent. of P^2O^5 requires

$$499.3 = 0.20\ (1.05\ X+1208.3)$$
$$X = \mathbf{1227}\text{ kg.}$$

The larger of these three amounts would be used, with 10 per cent. added to cover lime dust blown out, making 1350 kg. added, and the calculated composition of the slag:

CaO	1250 kg.	=	50.1 per cent.
MgO	723 "	=	2.9 "
SiO^2	286 "	=	11.4 "
P^2O^5	499 "	=	20.0 "
FeO	257 "	=	10.3 "
MnO	133 "	=	5.3 "
Total	**2497** "		

Recarburization.

When the bath has been blown to nearly pure iron, melted spiegeleisen is run in, to add the necessary carbon and manganese. Knowing the approximate composition and weight of the bath, and the composition of the melted spiegel, a simple arithmetical calculation would give the amount of the latter to be added, assuming no loss of carbon or manganese in the

operation. But experience shows that there is some loss, and that the carbon and manganese in the finished metal are always lower than the calculated amount. An interesting field is open here for calculating the loss of manganese and carbon and the amount of oxygen which must have been in the metal to cause these losses. A tabulation of many such calculations gives the metallurgist the necessary data for assuming the average amounts of carbon and manganese lost during recarburization, under different conditions of working, such as letting the metal stand before pouring or pouring at once, turning on the blast 5 or 10 seconds to mix up the bath, etc.

Problem 67.

At the end of the blowing the converter of Problem 65 contained 21,283 pounds of metal of the composition 0.04 per cent. carbon, 0.02 silicon, 0.01 manganese, 0.11 phosphorus, 0.06 sulphur, an unknown amount of oxygen (probably < 0.3 per cent.) and the rest iron. There is added to it 2,500 pounds of spiegeleisen, containing 4.64 per cent. carbon, 0.035 silicon, 14.90 manganese, and 0.139 phosphorus. The finished metal contained 0.45 per cent. of carbon, 0.038 silicon, 1.15 manganese, 0.109 phosphorus and 0.059 sulphur. Assume no iron oxidized.

Required: (1) A balance sheet of materials before and after recarburizing.

(2) The proportions of carbon and manganese going into the finished metal.

Solution: (1)

	Blown Metal	*Spiegel.*	*Steel.*	*Gases or Slag.*
C	8.5	116.0	106.5	18.0
Si	4.3	0.9	9.0	− 3.8
Mn	2.1	372.5	271.2	103.4
P	23.4	3.5	25.8	1.1
S.	12.8	....	14.0	− 1.2
Fe	21,232	2007	23,239	....

The differences in the sulphur, phosphorus and silicon are within the limits of error of the data, but there is no doubt as to the loss of carbon and manganese.

(2) The proportions of the two elements in question going into the finished steel are:

Carbon.....106.5÷124.5 = 0.85 = 85 per cent.
Manganese.....271.2÷374.6 = 0.72 = 72 "

The calculated percentages in the finished steel should have been, and actually were:

Carbon.....0.53 − 0.45, loss = 0.08 per cent.
Manganese.....1.58 − 1.15, loss = 0.43 "

Concerning oxygen removed, if we assume the loss of carbon and manganese to be due to their combining with oxygen dissolved in the bath, to form CO and MnO, the percentage of oxygen thus absorbed is:

By carbon.....0.08×16/12 = 0.11 per cent.
By manganese.....0.43×16/55 = 0.12 "

0.23 "

[The next chapter will consider the thermo-chemistry of the Bessemer process.]

CHAPTER VIII.

THERMO-CHEMISTRY OF THE BESSEMER PROCESS.

The feature of the Bessemer operation which strikes the observer as most wonderful, is that cold air is blown in great quantity through melted pig iron, and yet the iron is hotter at the end than at the beginning. If the observer will reflect a moment, however, he can see that if nothing but fuel, on fire, was in the converter, it would certainly be made much hotter by the air blast; in similar manner, the oxidation or combustion of part of the ingredients of the pig iron furnishes all the heat required for the process. Ten tons of pig iron contains, for example, some 350 kilograms, of carbon which is all burnt out in the bessemerizing, furnishing heat equal to the combustion of some 400 kilograms of coke—a not insignificant quantity, since it is burned and its heating power utilized in a very few minutes.

Elements Consumed.

The usual ingredients of pig iron are:

Iron	90.0	to	95.0	per cent
Carbon	2.5	"	4.5	"
Manganese	0.5	"	4.0	"
Silicon	0.5	"	4.0	"
Phosphorus	0.01	"	4.0	"
Sulphur	0.01	"	0.5	"

Some of the unusual constituents are nickel, chromium, titanium, aluminium, vanadium, tungsten, copper and zinc; all of these are rare, and there is seldom present as much as 0.5 per cent. of any one except in unusual cases.

In the Bessemer operation, carried out with the usual silica lining, iron, carbon, manganese and silicon are freely oxidized, but phosphorus and sulphur remain practically unchanged. In the basic Bessemer, lined with burnt dolomite and tar, phos-

phorus is also freely oxidized at the end of the operation, but sulphur is only slightly diminished—the more, the more manganese is in the slag. After all the oxidizable impurities are eliminated, iron itself oxidizes in much larger quantity, occasioning great loss if the blast is permitted to continue.

Iron oxidizes during the blow mostly to FeO, which enters the slag as ferrous silicate, and partly to Fe^2O^3. The brown fume which escapes in large amount if the blow is continued too long contains iron as Fe^2O^3.

Fe to FeO	1173	Calories per	kg. of Fe
Fe to Fe^2O^3	1746	" "	"
Fe to Fe^3O^4	1612	" "	"

The amount of iron oxidized can be gotten from the weight and percentage composition of the slag; also from the comparison of the weights of materials used and weight of ingots produced, knowing the weight of other impurities oxidized.

Carbon oxidizes mostly to CO gas, and partly, especially in the early part of the blow, to CO^2 gas. The proportion of each of these formed can only be known by analyzing the gases produced at various stages of the blow. The proportionate volumes of CO and CO^2 express the proportionate amounts of carbon forming each respective gas. A shallow bath allows more CO^2 to pass, on essentially the same principle that a deep layer of fuel on a grate favors the production of CO. The heat evolved by oxidation of carbon is:

C to CO	2430	Calories per	kg. of C
C to CO^2	8100	" "	"

Manganese oxidizes quickly and mostly to MnO. If the metal is a little overblown, Mn^2O^3 in small amount is found in the slag, while Mn^2O^3 is also present in the fumes. The heat evolved in these oxidations is:

Mn to MnO	1653	Calories per	kg. of Mn
Mn to Mn^2O^3	2480 (?)	" "	"

The last figure is estimated; it has not yet been determined experimentally.

Silicon oxidizes rapidly and early in the blow to SiO^2, forming silicate slag with the metallic oxides formed. Its heat

of oxidation has been usually taken as 7830 Calories per kilogram, but recent investigations have thrown doubt on this figure, Berthelot having found as low as 6414 Calories, and Mr. H. N. Potter, 7595 for crystalline silicon, equal to 7770 for amorphous silicon. Under these circumstances the best course is probably to use the middle value *ad interim*, and consider

Si to SiO^2.....7000 Calories per kg. of Si

We hope that the exact figure will soon be determined.

Phosphorus oxidizes to P^2O^5, and only towards the end of the blow. It is practically completely eliminated, going into the slag as calcium phosphate:

P to P^2O^5.....5892 Calories per kg. of P

Sulphur is not eliminated at all in the acid-lined converter. In the basic converter it is reduced in amount in the last few minutes, while phosphorus is disappearing, and partly escapes, mostly as SO^2 in the gases. The presence of a very basic slag is necessary, but the sulphur, while possibly going into the slag, does not remain there, but passes into the gases. The heat of oxidation of the unusual elements sometimes present are, as far as known,

Ni to NiO	1051	Calories per kg.	of Ni
Ti to TiO^2	4542	" "	Ti
Al to Al^2O^3	7272	" "	Al
Zn to ZnO	1305	" "	Zn
V to V^2O^5	4324	" "	V
W to WO^3	1047	" "	W
Cr to Cr^2O^3	2344	" "	Cr

Some of the above values are a little uncertain, and none of them include the heat of combination of the oxide formed with the slag.

Heat Balance Sheet.

Taking o° C. (32° F.) as a base line, we may express the total heat contents of the pig iron, steel, gases, slag, blast, etc.,

from this temperature. This method is simpler than to take the bath at any one high temperature and to reckon from there.

The items of heat available during the blow are:

Heat in the body of converter at starting.
Heat in the melted pig iron used.
Heat in the spiegleisen or ferro-manganese added.
Heat in hot lime added (sometimes in basic process).
Heat in the blast, if warm on entering.
Heat developed by oxidation of the bath.
Heat developed by formation of the slag.

The items of heat distribution are:

Heat in the body of the converter at finishing.
Heat in the steel poured.
Heat in the slag at finishing.
Heat in the gases escaping.
Heat in the fume.
Heat in the slag or metal blown out.
Heat absorbed in decomposing moisture of the blast.
Heat to separate the constituents of the bath.
Heat conducted away by supports, blast pipe, etc.
Heat conducted to the air in contact with converter.
Heat radiated during the blow.

These two columns should balance each other if all the items of each are correctly determined.

Heat in Converter Body at Starting.

If the converter were quite cold when the pig iron was run in and the blow started, this item would be zero. But such a case would result disastrously, since the heat absorbed by the converter during the blow would be more than any ordinary heat could afford to lose. It is, therefore, customary, when starting for the first time, to build a fire in the converter and turn on a little air blast, so as to bring the inside up to bright redness, say 900° to 1000° C. The outside shell would, under these conditions, be at about 200°, and the mean temperature of the converter lining, say 400°. If the converter were in regular operation, one charge being introduced as soon as the other was finished, then the heat in the body of the converter at starting could be practically regarded as equal to the heat in the

same at finishing, assuming the heats are running regularly An estimate of the heat in the converter body at starting is therefore only necessary when the converter is first started up, or when it is allowed to stand some time between blows.

Illustration: Assume a converter weighing, without charge, 25 tons, of which 5 tons is iron work and 20 tons silica lining. The mean specific heat of iron (for low temperatures) being $0.11012+0.000025t+0.0000000547t^2$, and for silica $0.1833+0.000077t$, calculate the heat contained in the body of the converter.—

(1) When the temperature of the outside shell is 200° and that of the lining averages 400° (converter warmed up for starting).

(2) When the temperature of the outside shell is 300° and that of the lining averages 725° (converter empty at end of a blow).

Solution: (1)

Heat in 5000 kg. of iron work:

$0.11012+0.000025\ (200)+0.0000000547\ (200)^2 = 0.11731$

$0.11731\times200\times5000 = 117,310$ Calories.

Heat in 20,000 kg. of silica lining:

$0.1833+0.000077\ (400) = 0.2141$

$0.2141\times400\times20,000 = 1,712,800$ Calories.

Total heat in converter body = 1,830,110 „

It may be remarked that this would require the consumption of at least 250 kilograms of coke, with a calorific power of 8,000 Calories, to warm the converter to this extent.

(2) Heat in 5,000 kg. of iron work:

$0.12354\times300\times5,000 = 185,310$ Calories.

Heat in 20,000 kg. of silica lining:

$0.2391\times725\times20,000 = 3,466,950$ „

Total = 3,652,260 „

This condition is assumed as representing the converter when just emptied and immediately refilled. In this case, in regular working, the heat in the converter body is practically the same at the beginning and at the end of a blow, and the heat losses through it are only those due to conduction to the air and ground and radiation.

Heat in Melted Pig Iron Used.

This quantity depends on the temperature at which the pig iron is run into the converter. If the iron is high in silicon, which would tend to produce a hot blow, it may be run in somewhat cool; but if low in silicon it should be run in much hotter. The minimum quantity of heat contained in a kilogram of melted pig iron may be put at 250 Calories; the maximum, for very hot pig iron, 350 Calories; about 300 Calories would be a usual average figure. This may be easily determined experimentally in any given case by granulating a sample in water in a rough calorimeter.

Heat in Metallic Additions.

Melted spiegeleisen is usually not very hot when run into the converter. It may contain 250 to 300 Calories per kilogram; say an average of 275. Ferro-manganese is sometimes added red-hot, at 800° to 900° C. At this temperature it would contain 120 to 135 Calories per kilogram, assuming a mean specific heat of 0.15.

Heat in Preheated Lime.

Taking the mean specific heat of CaO as $0.1715+0.00007t$, it would contain 154 Calories per kilogram at 700°, and 211 Calories at 900°. The heat content can be calculated for any known temperature at which the lime is used.

Heat in Warm Blast.

No Bessemer converters are run by hot blast, but the air pressure used is so great (20 to 35 pounds per square inch) that the blast is warmed by compression in the cylinders. If air at 1 atmosphere tension (ordinary air) be compressed to 2 or to 3 atmospheres tension, giving effective blast pressures of 1 to 2 atmospheres, the air is heated 60° or 103°, respectively, above its initial temperature. While some of this heat may be lost in the cylinder and conduits, yet the air, unless artificially cooled, passes to the tuyeres at 25° to 50° C. above the outside temperature, and thus imparts some heat to the converter.

Heat Developed by Oxidation.

We have already discussed the thermochemical data required for this calculation. To use the data we must find the weights

of each ingredient oxidized (not forgetting the iron itself) and the nature of the oxide it forms. This is deduced from the analysis of slag, gases and steel produced, as compared with those of the pig iron and additions used.

Heat of Formation of Slag.

The slag is a mechanical mixture or mutual solution of silicates of iron and manganese, with a little alumina (up to 5 per cent.) and lime and magnesia from nothing up to 5 per cent. In the basic process a large amount of calcium phosphate is present, representing over half of the entire slag, while magnesia is present in considerable amount, and alumina is almost absent.

Having, in the preceding column, calculated the heat of oxidation of all the metals oxidized in the converter, it remains to calculate the heat of combination of these to form slag. The silicate of alumina contributes nothing, since it occurred combined in the lining or lime added. The same can be said of the lime and magnesia in the acid process slags. The FeO and MnO are then to be considered, and the only thermochemical data we have are:

$(MnO, SiO^2) = 5{,}400$ Calories.
$(FeO, SiO^2) = 8{,}900$ "

These data are for 71 or 72 parts of MnO or FeO respectively, uniting with 60 parts of SiO^2. Since in acid slags there is always proportionately less of the bases, we should utilize the above heats of formation by expressing them per unit weight of MnO or FeO going into combination. These figures are:

Per kg. of MnO $= 5{,}400 \div 71 = 76$ Calories.
Per kg. of FeO $= 8{,}900 \div 72 = 124$ "

From these figures the heat of formation of the slag can be calculated: Any Fe^2O^3 present in the slag would be calculated as its equivalent weight of FeO (by multiplying by $144 \div 160$).

Illustration: A Bessemer slag contained by analysis:

SiO^2	47.25 per cent.
Al^2O^3	3.45 "
FeO	15.43 "
MnO	31.89 "
CaO, MgO	1.84 "

What is its heat of formation per kilogram?

Solution: The Al^2O^3, CaO and MgO are to be neglected, for reasons already given. The heat of combination, per kilogram of slag, is therefore,

FeO uniting with SiO^2 = 0.1543 × 124 = 19.1 Cal.
MnO uniting with SiO^2 = 0.3189 × 76 = 23.2 "
Total = 42.3 "

In basic Bessemer slags the conditions are much more complicated. The content of P^2O^5 is not under 14 per cent., runs as high as 25 per cent., and averages 19 per cent.; the CaO averages 45 per cent., limits 35 to 55; the silica is usually below 12 per cent., and averages 6 to 8 per cent.; magnesia is present from 1 to 7 per cent., average about 4 per cent. In such slags we should first of all assume the P^2O^5 to be combined with CaO as $3CaO.P^2O^5$, containing 168 of CaO to 142 of P^2O^5, (1,183 to 1) and having a heat of formation from CaO and P^2O^5 of 159,400 Calories per molecule, or 1123 Calories per unit weight of P^2O^5. Next the iron and manganese present may be calculated to FeO and MnO respectively, and treated as to their combination with SiO^2, the same as in an acid slag. Alumina may be considered in such basic slags as an acid, and equivalent to 120/102 of its weight of silica. These allowances will leave considerable lime and either an excess or deficiency of silica; if an excess, we can assume it combined with lime and magnesia, with a heat evolution equal to 476 Calories per kilogram of silica; if a deficiency, we let the calculations stand without further modification.

Illustration: Slag made at a Rhenish works contained:

SiO^2	7.73 per cent.
P^2O^5	21.90 "
Al^2O^3	3.72 "
Fe^2O^3	1.00 "
FeO	4.73 "
MnO	2.05 "
CaO	50.76 "
MgO	4.00 "
CaS	1.71 "

What is its heat of formation per unit of slag?

Solution: The 21.90 parts of P^2O^5 would be combined with $21.90 \times 168/142 = 25.91$ parts of CaO. This leaves 50.76—25.91 = 24.85 of CaO as either free, dissolved CaO or partly combined, in the slag. The 2.05 MnO would correspond to $2.05 \times 60/71 = 1.73$ SiO^2; the 4.73 FeO to $4.73 \times 60/72 = 3.94$ SiO^2; the 1.00 Fe^2O^3 to $1.00 \times 60/80 = 0.75$ SiO^2; a total SiO^2 requirement for these three bases of 6.42 per cent. The SiO^2 present is 7.73 per cent., adding to which the SiO^2 equivalent to the Al^2O^3 present ($3.72 \times 120/102 = 4.38$), we have 12.11 per cent. of summated silica. The ratio of summated FeO to summated SiO^2 is considerably below the ratio 72 to 60, we can, therefore, consider the summated FeO as all combined with silica. The summated FeO is:

FeO	= 4.73 per cent.
FeO equivalent of MnO	= 2.08 "
FeO equivalent of Fe^2O^3	= 0.90 "
	Total = 7.71 "

And the SiO^2 combining with this as $FeO.SiO^2$ is

$$7.71 \times 60/72 = 6.42 \text{ per cent.}$$

The excess of summated silica free to combine with lime is 12.11—6.42 = 5.69 per cent. As there is 24.85 of CaO and 4.00 of MgO for it to combine with, the heat of this combination must be calculated on the SiO^2 going into this combination.

We then have the formation heat of the slag as:

P^2O^5 to $3CaO . P^2O^5$	.....	$21.90 \times$	1123 =	24,594 Cal.
MnO to $MnO . SiO^2$	.....	$2.05 \times$	76 =	156 "
FeO to $FeO . SiO^2$	.....	$5.63 \times$	124 =	698 "
SiO^2 to $3CaO . SiO^2$	.....	$5.69 \times$	476 =	2,708 "
				28,156 "

This equals **281.6** Calories per unit weight of slag, forming a very important item in the heat balance sheet, particularly when the slag is large in amount.

Heat in Converter Body at Finishing.

This item reaches its maximum at the end of the blow, and would be equal to that calculated for the beginning of the blow,

with the exception that some of the lining, silica or dolomite has been corroded and passed into the slag, carrying with it its sensible heat.

Heat in Finished Steel.

This should be determined experimentally in each particular case. If not so determined an average value may be assumed, based on the following considerations: The finishing temperature averages 1650° C.; at this heat average Bessemer steel will contain a total of 350 Calories of heat per kilogram. If the temperature is determined by a pyrometer, a correction of 1/5 Calorie can be made for every degree hotter or colder than 1650°.

Heat in Slag.

Some experimental data are badly needed, concerning the heat in slags of different composition at different temperatures. At present it is necessary to make guesses, wherever the heat in the slag produced is not directly determined. At a finishing temperature of 1650° it is likely that the slag contains 550 Calories per kilogram; with a variation of 1/4 Calorie for each degree hotter or colder than 1650°.

Heat in Escaping Gases.

The amount of these gases can only be determined satisfactorily from their analysis and the known weights of carbon oxidized. Direct estimation from the piston displacement is of much less exactness, because the slip and leakage at these high pressures may reach 25 to 50 per cent. or even more. The temperature of the gases is only slightly less than that of the bath, that is, some 1350° at starting and 1650° at finishing. Outside in the air the Bessemer flame may be much hotter than this, but that is due to further combustion of CO to CO^2 outside the converter, and should be disregarded. Where extra air is blown upon the surface of the bath, as in " baby " converters, it is quite possible that the gases in the converter and the escaping gases may be considerably hotter than the bath itself These variations must be taken into consideration. The most satisfactory condition is to insert a pyrometer tube into the opening of the converter and measure the temperature directly. The heat carried out by the gases can then be calculated ac-

curately, using the proper mean specific heats to these high temperatures already used in these calculations.

Heat in Escaping Fume.

This is mostly oxides of iron and manganese, with sometimes silica. It is relatively small in amount. Its quantity being known, consider it at the same temperature as the gases, with a mean specific heat of 0.40 if free from silica, and 0.35 if siliceous.

Heat in Slag or Metal Blown Out.

These can be counted as equal to the heat in an equal quantity of slag or metal at the finishing temperature.

Heat Absorbed in Decomposing Moisture.

Knowing the amount of moisture blown in with the blast, a proper allowance is $29{,}040 \div 9 = 3{,}227$ Calories for every kilogram of moisture thus blown in. It is probable that this moisture is all decomposed, its hydrogen appearing in the gases. In the absence of data as to the hygrometric condition of the blast, the amount of moisture entering may be inferred and calculated from the amount of hydrogen in the gases.

Heat to Separate Constituents of Bath.

We here meet the question, how much heat of combination exists between the bath and the various ingredients which are removed—carbon, silicon, manganese, phosphorus, sulphur. Le Chatelier believes manganese to exist in the bath as Mn^3C, requiring 80 Calories per kilogram of manganese to decompose it. Silicon and carbon have, as far as has at present been determined, no sensible heat of combination with iron. Sulphur requires 750 Calories to separate each kilogram from iron. Phosphorus requires, according to Ponthiere, 1397 Calories to separate each kilogram from iron, but the reliability of this datum is doubtful. Until more reliable tests are made it is perhaps better to omit this item than to use it, although it must be of great importance if as large as Ponthiere states it to be.

Heat Conducted Away by Supports.

This is a very difficult quantity to determine, being conditioned by the size of the supports, their cooling surface and

the kind of connection they have with other objects. The heat which would pass to the blast pipe is practically returned to the converter by the incoming blast. The heat passing into the supports is perhaps best found by taking their temperature at different places, and calculating the heat loss from their surface by radiation and conduction to the air. This amounts practically to considering them as part of the outer cooling surface of the converter; the calculation of these surface losses is given in the two following paragraphs:

Heat Conducted to the Air.

This is a function of the extent of outside surface, its temperature, the temperature of the air, and the velocity of the air current. Measurement will give the extent of surface in contact with the air and the average velocity of the air current; the surface being rough iron, the coefficient of transfer conductivity may be taken as $k = 0.000028\ (2 + \sqrt{v})$. where v is the air velocity in c.m. per second, and k is the heat conducted per second in gram-calories, from each square c.m. of surface per 1° difference of temperature. The temperature of the outer surface should be carefully measured, so that a reliable average is obtained, and the air velocity likewise averaged, since it has considerable influence on the heat lost to the air.

Illustration: A converter has an outside surface of 50 square meters, at an average temperature during the blow of 200° C. the average air current being 1 meter per second, and outside air 30° C. What is the heat loss by conduction to the air in kilogram Calories per minute?

Solution:

Coefficient of transfer conductivity:

$$0.000028\ (2+\sqrt{100}) = 0.000336\,.$$

Heat loss per 1° difference, per second, in gram-calories:

$$50\times 10{,}000\times 0.000336 = 168 \text{ calories.}$$

Heat loss per 170° difference, per minute, in kg.-calories:

$$168\times 170\times 60\div 1000 = \mathbf{1714} \text{ calories.}$$

Heat Radiated During the Blow.

This is a function of the temperature of the outside shell, the mean temperature of the surroundings of the converter and the nature of the metallic surface. As the surface is oxidized iron, it would lose about 0.0141 gram-calories from each square centimeter per second, if at a temperature of 100° and the surroundings at 0°; or practically 1 gram-calorie per second from each square meter, for every 100,000,000 of numerical difference between the fourth powers of the absolute temperature of the radiating surface and its surroundings. (See Metallurgical Calculations, Part 1., p. 185).

Illustration: Assuming the surroundings of the converter at 30°, in the preceding illustration, what amount of heat is radiated per minute in large Calories?

Solution: The absolute temperatures in question are $273+30 = 303$, and $273+200 = 473$. The difference of their fourth powers is:

$$473^4 - 303^4 = 41{,}626{,}500{,}000,$$

which, divided by 100,000,000, gives 416.265 gram-calories lost per second per each square meter of radiating surface. The radiation loss for the whole surface per minute is, therefore:

$$416.265 \times 50 \times 60 \div 1000 = \mathbf{1249} \text{ kg.-Calories.}$$

While the assumption made as to the temperature of the outside shell is doubtless only approximate, yet if the temperature of the same is carefully determined the radiation loss can be accurately calculated. If the outside of the converter were polished, this radiation loss might be reduced nearly nine tenths.

Problem 68.

From the data and results of calculation of Problem 65 (see pages 310, 317 and 323,) we see that 22,500 pounds of pig iron and 2,500 pounds of spiegeleisen produced 24,665 pounds of steel, there being eliminated during the blow and recarburization:

Carbon	679.5	pounds (140.7 to CO^2)
Silicon	203.2	"
Manganese	197.9	"
Iron	253.9	" (25.3 to Fe^2O^3)

The gases contain:

CO^2	5.20	per cent.
CO	19.91	"
H^2	1.39	"
N^2	73.50	"

The slag contains:

SiO^2	63.56	"
Al^2O^3	3.01	"
FeO	21.39	"
Fe^2O^3	2.63	"
MnO	8.88	"
CeO	0.90	"
MgO	0.36	"

Make average assumptions for requisite data not given.

Required: A balance sheet of heat evolved and distributed.

Solution: The items of this balance sheet have already been discussed in detail. We will apply them to this specific case:

Heat in Body of Converter at Starting: Assuming that this is a blow in regular running, the heat may be taken at any reasonably approximate quantity, because the same quantity with only a slight deduction will be allowed as contained in the same on finishing. We will, therefore, take a figure already calculated, 8,034,970-pound Calories, as the heat in the converter body at starting.

Heat in Melted Pig Iron: We will take it at 300 Calories per pound, or a total of $300 \times 22,500 = 6,750,000$ Calories.

Heat in Spiegeleisen: $2,500 \times 300 = 750,000$ Calories.

Heat in Blast: This may safely be considered as warmed by compression and entering the converter at 60° C. The amount of blast received altogether is calculated thus:

Carbon oxidized = 679.5 pounds.

Volume of CO and CO^2 formed:

$$679.5 \times 16 \div 0.54 = 20,133 \text{ cu. ft.}$$

Volume of gases $\frac{20,133}{0.2511}$ = 80,179 "

Volume of nitrogen $80,179 \times 0.735$ = 58,932 "

Volume of air proper in blast = 74,408 "

Volume of hydrogen in gases:

$80,179 \times 0.0139 = 1,115$ "

Volume of moisture in gases = 1,115 "

Assuming the blast at 60° C., the heat in it is:

Air	74,408×0.3046	=	22,665 oz. Cal. per 1°
H^2O	1,115×0.3790	=	423 " "
			23,088 " "
	23,088×60	=	1,385,280 oz. Cal.
		=	86,580 lb. Cal.

Heat of Oxidation:

C to CO^2	140.7×8100	=	1,139,670 Calories
C to CO	538.8×2430	=	1,309,280 "
Si to SiO^2	203.2×7000	=	1,422,400 "
Mn to MnO	197.9×1653	=	327,130 "
Fe to FeO	228.6×1173	=	268,150 "
Fe to Fe^2O^3	25.3×1746	=	44,170 "
			4,510,800 "

Heat of Formation of Slag: The 197.9 pounds of manganese oxidized forms 255.5 of MnO. Hence the weight of the slag is 255.5÷0.0888 = 2877 pounds. The slag, therefore, contains also 2877×0.6356 = 1829 pounds of SiO^2, of which 203.2 ×60/28 = 435 pounds came from the silicon oxidized, and 1794 pounds from the lining. The lining will also have lost the Al^2O^3, CaO and MgO in the slag, equal to 2877 × 0.0427 = 123 pounds. The total iron going into the slag, 253.9 pounds, is equivalent to 326.4 pounds of FeO.

The heat of formation of the slag will therefore be:

FeO	326.4×124	=	40,474 Calories.
MnO	255.5× 76	=	19,418 "
	Total		59,892 "

Heat in Converter at Finishing: This will be the same as at starting, less the heat in 1794+123 = 1917 pounds of lining, which was corroded and entered the slag. Assuming this to have been on the inner surface, at an average temperature of 1500°, the heat in it, using the mean specific heat of silica, will have been

$$1917 \times 0.2988 \times 1500 = 851{,}200 \text{ Calories.}$$

And the heat in the converter body at the finish:

$$8{,}034{,}970—851{,}200 = 7{,}183{,}770 \text{ pound Calories}$$

Heat in Finished Steel: Taking its temperature as 1650°, with 350 Calories per unit, we have

$$24{,}665 \times 350 = 8{,}632{,}750 \text{ Calories.}$$

Heat in the Slag:

$$2877 \times 550 = 1{,}582{,}350 \quad \text{“}$$

Heat in Escaping Gases: These have already been calculated as consisting of

Nitrogen	58,932	cubic feet.
Hydrogen	1,115	“ “
Carbon monoxide	15,964	“ “
Carbon dioxide	4,169	“ “

The first three have the same heat capacity per cubic foot, so assuming their temperature 1550°:

N^2, H^2, CO	$76{,}011 \times 534.5$	= 40,627,900	oz. Cal.
CO^2	$4{,}169 \times 947.1$	= 3,948,250	“
			“
		44,576,150	“
		= 2,786,000	lb. Cal.

Absorbed in Decomposing Moisture: The 1,115 cubic feet of hydrogen in the gases represent so much steam or water vapor decomposed. Since 1 cubic foot = 0.09 ounces, the heat absorbed is

$$1{,}115 \times 0.09 \times 29{,}040 = 2{,}914{,}160 \text{ oz. Cal.}$$
$$= 182{,}130 \text{ lb. Cal.}$$

Heat Conducted to the Air: Assuming the conditions worked out in the illustration under this heading, this item would be approximately, for 9 min. 10 secs., in lb. Cal.

$$1{,}714 \times 2.204 \times 9.167 = 34{,}630 \text{ lb. Cal.}$$

Heat Lost by Radiation: Making similar assumption, we have

$$1{,}249 \times 2.204 \times 9.167 = 25{,}240 \text{ lb. Cal.}$$

Recapitulation.

	Lb. Cal.
Heat in converter body at starting	8,034,970
" melted pig-iron	6,750,500
" spiegeleisen	750,000
" blast	86,580
Heat of oxidation	4,510,800
" formation of slag	59,890
Total on hand and developed	20,192,740
Heat in converter body at finish	7,183,770
" finished steel	8,632,750
" slag	1,582,350
" escaping gases	2,786,000
Heat absorbed in decomposing moisture	182,130
Heat conducted to the air	34,630
Heat lost by radiation	25,240
Total accounted for	20,426,870

Another way of expressing this balance is to itemize the avenues of heat evolution and utilization, as follows:

	Lb. Cal.
Received from converter body	851,200
Received by oxidation	4,510,800
Received by formation of slag	59,890
Total	5,421,890

	Lb. Cal.
Used, excess of heat in gases over blast	2,699,420
Used, excess of heat in steel and slag over pig iron and spiegel	2,714,600
Decomposition of moisture	182,130
Radiation and conduction	59,870
Total	5,656,020

CHAPTER IX.

THE TEMPERATURE INCREMENT IN THE BESSEMER CONVERTER.

In the preceding chapter, we have studied the generation of heat in the Bessemer converter, and its distribution. We saw in that analysis that in a typical operation, nearly one-half of the heat generated during the blow is carried out by the hot gases, about half is represented in the increased temperature of the contents of the converter, while only about 5 per cent. is lost by radiation, etc. In the present paper we wish to analyze still further this question of increased temperature, which is so vitally necessary for the proper working of the process, and to calculate the relative efficiency of the various substances oxidized in causing this rise of temperature.

While at no time in the Bessemer operation is only one substance being oxidized, yet we can get the best basis for our computations by assuming a charge in operation and only one substance oxidized at a time. Whatever substance is in question, let us assume one kilogram burnt in a given short period of time, generating the heat of its combustion. With the bath at a given temperature, the air, at say 100° C., comes in contact with it, bearing the necessary oxygen. If nothing was oxidized, the oxygen and nitrogen would simply be heated to the temperature of the bath, and pass on and out, while the bath would be meanwhile losing heat also by radiation. It is evident then, that unless at least as much heat as the sum of these two items is generated, the bath will cool, and that only the excess of heat above this requirement is available for increasing the temperature of the bath and resulting gases. The proper procedure for us will therefore be to calculate, in each case, the chilling effect of the air entering, subtract this from the heat generated, and the residue is net heat available for raising the temperature of the contents of the con-

verter and the gases, and supplying radiation losses. The latter are proportional to the time, and therefore to the amount of air used, assuming blast constant.

Silicon.

This is burnt out in the first part of the process, during which the temperature begins low and ends high. We will therefore assume two temperatures, and calculate the thermal increment at each. We will take 1250° and 1600°. The net heat is absorbed by the bath, slag and nitrogen.

Oxygen necessary to burn one kilogram of silicon:

$1 \times 32 \div 28 =$	1.143	kg.
Nitrogen accompanying this oxygen	= 3.810	"
Weight of air needed	= 4.953	"
Volume of air = $4.953 \div 1.293$	= 3.831	m^3
Specific heat, 100° to 1250°, per m^3	= 0.3395	
Specific heat, 100° to 1600°, per m^3	= 0.3489	
Chilling effect of air at 100°, bath at 1250°		
$= 3.831 \times 0.3395 \times 1150$	= 1496	Cal.
Chilling effect of air at 100°, bath at 1600°		
$= 3.831 \times 0.3489 \times 1500$	= 2043	Cal.
Heat generated per kilogram of silicon	= 7000	Cal.

This is, however, for cold oxygen and cold silicon burning to cold solid silica. Under the conditions prevailing we have melted silicon at the temperature of the bath, oxidized by hot oxygen to hot silica, giving a slightly different heat of combination, calculated as follows:

Heat in melted silicon at 1250°	= 480	Cal.
" " oxygen required, at 1250°	= 334	"
" " silica, at 1250°	= 750	"
Heat of oxidation at 1250°		
$= 7{,}000 + 480 + 334 - 750$	= 7,064	"

The difference from 7,000 is so small as to be within the possible error of the 7,000 itself, and we can therefore make the calculations with all the accuracy they allow, taking the ordinary heats of oxidation from the tables.

One factor of heat generation has, however, not been mentioned, viz.: the heat of combination of silica with oxides of

iron and manganese to form slag. This is 148 Calories per kg. of silica when forming iron silicate, and 90 when forming manganese silicate, which quantities would become 317 and 193 Calories respectively when calculated per kg. of silicon oxidizing. The question arises, however, whether it is fair to credit all this to the silica, because this generation of heat by slag formation is really a mutual affair, chargeable to the credit of both silica and the other oxides; we should, therefore, not charge it all up to the credit of silica formation, and we do not know what part to charge to the credit of silica if we do not charge it all. In this dilemma it may be well to remember that silicon is probably oxidized before the iron and manganese, and that the heat of formation of the slag is therefore more properly considered as being generated afterwards, and therefore may be practically credited entirely to the oxidation of iron and manganese.

Resume for oxidation of 1 kilo. of silicon:

	Cal.
Heat generated	= 7,000
Chilling effect of the blast, 100° to 1250°	= 1,496
Chilling effect of the blast, 100° to 1600°	= 2,043
Available heat, bath at 1250°	= 5,504
Available heat, bath at 1600°	= 4,957

If we assume a radiation loss proportional to the length of the blow, *i. e.*, proportional to the air blown in, we can find out from average blows that this amounts to about 50 Calories per cubic meter of blast used. The radiation loss during combustion of 1 kilogram of silicon would therefore be

	Cal.
3.831×50	= 192
Leaving net available heat at 1250°	= 5,312
At 1600°	= 4,765

The above quantity of heat is expended in raising the temperature of 99 kg. of bath, 2.143 kg. of silica, and 3.810 kg. of nitrogen gas, from their initial temperature. At the temperatures of 1250° and 1600°, respectively, the heat capacity of these products of the operation will be, per 1° C. rise:

Products.	*Specific Heat* at 1250°	at 1600°	*Heat Capacity* at 1250°	at 1600°
Bath, 99 kg.....	0 25	0.25	24.8	24.8
SiO^2, 2.14 kg.....	0.37	0.43	0.8	0.9
N^2, 3.02 m^3.....	0.37	0.39	1.1	1.2
		Totals.	26.7	26.9

Theoretical rise of temperature:

5,312 ÷ 26.7 = 199° (bath at 1250°)
4,765 ÷ 26.9 = 177° (bath at 1600°)

Average rise, per average 1% of silicon = 188° C.

Manganese.

As high as 4 per cent. of manganese may be oxidized during the blow, and therefore this heat of combustion is sometimes important. We will calculate the net heat available for raising temperature and the rise of temperature per 1 per cent. of manganese oxdized, *i. e.*, for 1 kilo. of manganese per 100 kilos. of bath.

Oxygen necessary 1×16/55	= 0.291 kg.
Nitrogen accompanying this	= 0.970 "
Weight of air used	= 1.261 "
Volume of air used	= 0.975 m^3
Chilling effect of air at 100° on bath at 1250° = 0.975×0.3395×1150	= 381 Cal.
Heat generated per kg. of manganese	= 1653 "
Heat of formation of $MnO.SiO^2$ 1.291 kg. MnO×76	= 98 "
Total heat developed	= 1751 "
Heat available = 1751—381	= 1370 "
Radiation loss = 0.975×50	= 49 "
Net available heat	= 1321 "
Heat capacity of 99 kg. of bath per 1°	= 24.8 "
Heat capacity of 2.4 kg. of slag	= 0.7 "
Heat capacity of 0.8 m^3 nitrogen	= 0.3 "
Heat capacity of products per 1°	= 25.8 "

Theoretical rise of temperature:

$$1321 \div 25.8 = 51° \text{ C.}$$

This is, in round numbers, one-fourth the efficiency of silicon.

Iron.

While it is not desired to oxidize iron, and while it is relatively less oxidizable than silicon or manganese, yet some is always oxidized because of the great excess of iron present in the converter. The amount of iron thus lost is variable, and some of it, towards the end of the blow, may be oxidized to Fe^2O^3 instead of FeO, the larger part, however, oxidizes to FeO. We will make the calculations for both oxides, per kilogram of iron.

Formation of FeO.

Oxygen necessary $1 \times 16/56$	= 0.286	kg.
Nitrogen accompanying this	= 0.953	"
Weight of air used	= 1.239	"
Volume of air used	= 0.958	m^3
Chilling effect of air at 100° on bath at 1250° = $0.958 \times 0.3395 \times 1150$	= 374	Cal.
Chilling effect of air at 100° on bath at 1600° = $0.958 \times .3489 \times 1500$	= 501	"
Heat generated per kg. of iron	= 1,173	"
Heat of formation of $FeO.SiO^2$ = 1.286 kg. FeO × 124	= 159	"
Total heat developed	= 1,332	"
Net heat available at 1250° = 1332—374	= 958	"
Net heat available at 1600° = 1332—501	= 821	"
Radiation losses = 0.958×50	= 48	"
Net available heat at 1250°	= 910	"
Net available heat at 1600°	= 773	"
Heat capacity of 99 kg. of bath per 1°	= 24.8	"
Heat capacity of 2.4 kg. of slag per 1°	= 0.7	"
Heat capacity of 0.8 m^3 of nitrogen	= 0.3	"
Heat capacity of products per 1°	= 25.8	"

Theoretical rise of temperature:

$$910 \div 25.8 = 36° \text{ C.}$$
$$773 \div 25.8 = 30° \text{ C.}$$

This is only about one-sixth as efficient as silicon.

Formation of Fe^2O^3.

Weight of air used	= 1.859	kg.
Volume of air used	= 1.438	m^3
Chilling effect of air at 100° on bath at 1600° = 1.438×0.3489×1500	= 753	Cal.
Total heat developed by oxidation	= 1746	"
Heat of formation of slag	= 159	"
Total heat developed	= 1905	"
Heat available = 1905—753	= 1152	"
Radiation losses = 1.438×50	= 72	"
Net heat available	= 1080	"
Heat capacity of products	= 26	"

Theoretical rise of temperature:

$$1080 \div 26 = \mathbf{42}^\circ \text{ C.}$$

TITANIUM.

While titanium is an unusual constituent of pig iron, yet it is conceivable that titaniferous pig iron might be made and blown to steel. If so, the following calculation, based on a quite recently determined value for the heat of oxidation of titanium, will show that the titanium is a valuable heat producing substance, being, in fact, weight for weight three fourths as efficient as silicon.

Oxygen needed 1×32/48	= 0.667	kg.
Nitrogen accompanying this	= 2.222	"
Air used	= 2.888	"
Volume of air needed	= 2.250	m^3
Chilling effect of air at 100° on bath at 1250° = 2.250×0.3395×1150	= 878	Cal.
Heat generated per kg. of Ti	= 4542	"
Heat of formation of slag—unknown		
Net heat available = 4542—878	= 3664	"
Deducting 144 for radiation losses	= 3520	"
Heat capacity of products per 1° C.	= 26.5	"

Theoretical rise of temperature:

$$3520 \div 26.5 = \mathbf{133}^\circ \text{ C.}$$

Aluminium.

This metal is also rarely found in pig iron, yet when present it would be a powerful heat producer, as the following calculations show:

Oxygen needed $1 \times 48/54$	= 0.889 kg.
Nitrogen	= 2.963 "
Air	= 3.852 "
Volume of air	= 2.964 m^3
Chilling effect of air at 100° on bath at 1250° = $2.964 \times 0.3395 \times 1150$	= 1157 Cal.
Heat generated per kg. of Al	= 7272 "
Heat of formation of slag—uncertain	
Heat available = 7272—1157	= 6115 "
Deducting for radiation losses	= 5967 "
Calorific capacity of products per 1° C.	= 26.6 "

Theoretical rise of temperature:

$$5967 \div 26.6 = 224° \text{ C.}$$

If a blow was running cold, and ferro-silicon was not on hand to add in order to increase its temperature, ferro-aluminium, or aluminium itself, would be a good substitute in the emergency.

Nickel.

It is hardly probable that nickeliferous pig iron would be blown to steel, because of the waste of valuable nickel in the slag; yet if 1 per cent. of nickel were thus oxidized, calculations similar to the preceding would show a net rise in temperature of the contents of the bath of about 33° C.

Chromium.

Quite recently some chromiferous pig iron has been blown in the Bessemer converter, and those in charge were hampered by the lack of data as to how chromium would behave during the blow and its heat value to the converter, Technical literature will probably soon contain an account of the practice which has been developed at the Sparrow's Point works of the Maryland Steel Company. No thermo-chemist has, as yet, determined the heat of formation of chromium slag. From

what we know of the chemical reactions of chromium it is likely that this heat is considerable. Neglecting the heat of formation of slag, we have the following approximation to its heating efficiency, assuming it to be oxidized when the bath is near to its maximum temperature:

Oxygen needed $1\times48/104$	= 0.462 kg.
Nitrogen entering	= 1.540 "
Air used	= 2.002 "
Volume of air	= 1.548 m^3
Chilling effect of air at 100° on bath at 1600° = $1.548\times0.3489\times1500$	= 810 Cal.
Heat of oxidation	= 2,344 "
Net heat = 2344—810	= 1,534 "
Deducting for radiation losses	= 1,457 "
Calorific capacity of products per 1°	= 26.1 "

Theoretical rise of temperature:

$$1457\div26.1 = 56^\circ \text{ C.}$$

Carbon.

This element commences to be oxidized in large amount only towards the middle of the blow, when the temperature of the bath is high, because of the previous oxidation of silicon. It will be about right, therefore, to estimate the bath at an average temperature of 1600° during the elimination of carbon. The product is mostly CO, but partly CO^2. We will, therefore, calculate for each of these possible products separately. The net heat available, after allowing for average radiation losses, is used to increase the temperature of the products, *i. e.*, of the bath, the nitrogen and the CO or CO^2.

Oxidation to CO^2.

Oxygen required = $1\times32/12$	= 2.667 kg.
Nitrogen accompanying	= 8.889 "
Air used	= 11.556 "
Volume of air	= 8.937 m^3
Chilling effect of air at 100° on bath at 1250° = $8{,}937\times0.3395\times1150$	= 3,489 Cal.
Heat of oxidation	= 8,100 "

Heat available = 8,100—3,489	=	4,611 Cal.
Radiation losses = 8.937×50	=	447 "
Net heat available	=	4,164 "
Heat capacity of 99 kg. bath = 99×0.25	=	24.80 "
Heat capacity of 7.05 m^3 N^2 = 7.05×0.37	=	2.61 "
Heat capacity of 1.90 m^3 CO^2 = 1.90×0.88	=	1.70 "
Heat capacity of products, per 1° C.	=	29.11 "

Theoretical rise of temperature:

$$4{,}164 \div 29.11 = \mathbf{143}°\text{C.}$$

Since carbon burns to CO^2 principally at the beginning of the blow, while the bath is cold, we see that carbon thus consumed is about three-quarters as efficient as an equal weight of silicon in raising the temperature of the bath.

Oxidation to CO.

Oxygen needed $1 \times 16/12$	=	1.333 kg.
Nitrogen accompanying	=	4.444 "
Air used	=	5.777 "
Volume of air	=	4.469 m^3
Chilling effect of air at 100° on bath at 1600° = $4.469 \times 0.3489 \times 1500$	=	2,339 Cal.
Heat of oxidation	=	2,430 "
Heat available = 2,430—2,339	=	91 "
Radiation losses = 4.469×50	=	233 "
Net heat available = 91—233	=	—142 "
Heat capacity of 99 kg. of bath = 99×0.25	=	24.8 "
Heat capacity of 3.5 m^3 of N^2 / Heat capacity of 1.9 m^3 of CO } 5.4×0.39	=	2.1 "
Heat capacity of products	=	26.9 "

Theoretical rise of temperature:

$$-142 \div 26.9 = -\mathbf{5}° \text{ C.}$$

The result is, therefore, that when carbon burns, as it mostly does, to CO, and the temperature of the bath is high, there is practically no further rise of temperature, for the heat of oxidation is barely sufficient to counteract the chilling effect of the air and to supply radiation and conduction losses.

In the above calculations, no allowance was made for heat

required to separate carbon from its combination with iron, or for the variation in the heat of combination of carbon with oxygen from the combination heats at ordinary temperatures. The former is not known, or perhaps is very nearly zero. The heat of oxidation of liquid carbon at 1250° to CO^2 or at 1600° to CO is calculated as follows:

Oxidation 1 kg. C to CO^2 at 0°		= 8,100 Cal
Heat to raise 1 kg. C to 1250°	= 505 Cal.	
Heat to liquefy 1 kg. at 1250°	= 129 "	
Heat to raise 2.67 kg. O^2 to 1250°	= 779 "	
Heat to raise reacting substance to 1250°		= 1,413 "
Heat in 3.67 kg. CO^2 at 1250°		= 1,493 "
Heat of reaction at 1250° (8,100+1,413−1,493)		= **8,020** "

For production of CO, at 1600°, the correction is larger, as is seen from the following:

Oxidation 1 kg. C to CO at 0°		= 2,430 Cal.
Heat to raise 1 kg. to 1600°	= 680 Cal.	
Heat to liquefy 1 kg. C at 1600°	= 156 "	
Heat to raise 1.33 kg. O^2 to 1600°	= 554 "	
Heat to raise reacting substances to 1600°		= 1,390 "
Heat in 2.33 kg. of CO at 1600°		= 1,104 "
Heat of reaction at 1600° (2,430+1,390—1,104)		= **2,716** "

The use of this corrected value makes the oxidation of C to CO give a small net heat development, with consequent slight rise of temperature, instead of the slight cooling effect before calculated. The conditions are so nearly even, however, that a slight increase of temperature or slowing up of the blow would wipe out the heat excess.

Phosphorus.

This is the last important element to be considered, and is always eliminated after the carbon, at the maximum bath temperature, which we will assume, for calculation, at1600°. The heat generated, at ordinary temperatures, is 5892 Calories per kilogram of solid phosphorus. Per kilogram of liquid phosphorus it would be only 5 Calories more, or 5897 Calories. For the reaction at 1600° we would have a different value, probably

some 500 Calories more, but the necessary data concerning the specific heats of P and P^2O^5 are not known, and we must omit this calculation. The heat of combination of iron and phosphorus is also a doubtful quantity. Ponthiere places it as high as 1,397 Calories per kilogram of phosphorus, but this appears altogether improbable since another experimenter could obtain no heat of combination at all. As concluded in another place, I advise for the present omitting this questionable quantity.

The phosphorus pent-oxide forms $3CaO \cdot P^2O^5$ with the lime added, but since there is always more lime present than corresponds to these proportions ($3CaO : P^2O^5 :: 168 : 142$), the calculation of heat of formation of the slag must be based on the amount of P^2O^5 formed (1123 Calories per kilogram of P^2O^5). This amounts to a considerable item. On the other hand, the lime needed for slag is put in, usually preheated, for the sole purpose of combining with the P^2O^5. It seems, therefore, only right to charge the phosphorus with the heat required to raise this lime to the temperature of the bath. The lime added averages three times the weight of P^2O^5 formed, and is preheated usually to about 600°. Assuming these conditions, the following calculations can be made per kilogram of phosphorus oxidized:

Oxygen required	=	1.29 kg.
Nitrogen accompanying	=	4.30 "
Air used	=	5.59 "
Volume of air	=	4.32 m^3
Heat of formation of slag, 2.29 kg. $P^2O^5 \times 1123$	=	2572 Cal.
Heat of oxidation of phosphorus	=	5897 "
Total heat developed	=	8469 "
Chilling effect of air at 100° on bath at 1600° = $4.32 \times 0.3489 \times 1500$	=	2261 "
Chilling effect of lime (600° to 1600°) $(2.29 \times 3) \times 0.328 \times 1000$	=	2253 "
Chilling effect of blast and lime	=	4514 "
Heat available = 8469—4514	=	3955 "
Radiation losses = 4.32×50	=	216 "
Net heat available	=	3739 "

Heat capacity 99 kg. of bath = 99×0.25	=	24.8 kg.
Heat capacity 3.4 m^3 of N^2 = 3.4×0.39	=	1.3 "
Heat capacity 6.9 kg. of slag = 6.9×0.3	=	2.1 "
Heat capacity of products, per 1°	=	28.2 "

Theoretical rise of temperature:

$$3739 \div 28.2 = \mathbf{133}^\circ \text{ C.}$$

If the lime were added cold, its cooling effect would be 883 Calories greater, the net heat available would be 883 Calories less, and the calculated rise of temperature 31° less, or 102° C. Using the preheated lime we can regard phosphorus as being practically two-thirds as efficient, weight for weight, as silicon; with cold lime, about one-half as efficient.

RESUME.

Heat effect of oxidizing 1 kilogram of element.

	Heat of Oxidation.	*Formation of Slag.*	*Total Heat Developed.*	*Chilling Effect of Blast, Radiation, etc.*	*Net Heat Available for Raising Temperature.*	*Theoretical Rise of Temperature.*
Silicon	7,000	...	7,000	1,688	5,312	188°
Manganese	1,653	98	1,751	430	1,321	51°
Iron (to FeO)	1,173	159	1,332	422	910	33°
Iron (to Fe_2O_3)	1,746	159	1,905	825	1,080	42°
Titanium	4,542	...	4,542	1,022	3,520	133°
Aluminium	7,272	...	7,272	1,305	5,967	224°
Nickel	1,051	159	1,210	378	832	33°
Chromium	2,344	. .	2,344	887	1,457	56°
Carbon (to CO_2)	8.100	...	8,100	3.936	4,164	143°
Carbon (to CO)	2,430	.	2,430	2,572	−142	—5°
Phosphorus	5,897	2,572	8,469	2,477 2,253*	3,739	133°

* Chilling effect of lime added, preheated to 600°

It must be observed that the above table is for comparison only, it cannot be used for an actual case, such as when 1 per cent. of silicon, 3 of iron, 4 of carbon and 2 of phosphorus are

oxidized. In such a case, the rise in temperature would be only very roughly:

From silicon	1×188	= 188°
From iron	3×33	= 99°
From carbon	– say	= 0°
From phosphorus	2×133	= 266°
Total		= 553° C.

It is to be recommended that in each specific case the calculation be made for the specific conditions obtaining, such as temperature of the metal at starting, temperature of the blast, time of the blow (as far as this affects radiation and conduction losses), proportion of carbon burned to CO^2, free oxygen in the gases, moisture in the blast, temperature and quantity of lime added, corrosion of lining. When all these items and conditions are taken into account there will be room for only small discrepancy between the calculated and the observed rise of temperature. The chief items needing experimental research at present are: The specific heat of the melted bath, the specific heat of the slag, the heat of combination of various elements comprising the bath, the heat of formation of the slag, and the heat of oxidation of some of the rarer elements. Such establishments as the Carnegie Institution could not do the cause of metallurgy better service than to subsidize metallurgical laboratories for the determination of such data.

CHAPTER X.

THE OPEN-HEARTH FURNACE.

By the above title we mean to designate not only the regenerative gas furnaces for making steel but also those for reheating purposes; in other words, regenerative or recuperative reverberatory furnaces. Prominent among these is the Siemens-Martin furnace, with complete gas and air preheating regenerative chambers. In all these furnaces the charge is heated, or kept hot, partly by direct contact with the gaseous products of combustion and partly by radiation from the flame and the sides and roof of the furnace. It was the Siemens brothers who first insisted on the relatively great importance of the radiation principle, in distinction to the direct impingement of the flame on the material, pointing out that a luminous flame radiates from all parts of its volume, while a hot, solid body radiates only from its surface, and direct impingement interferes with the development of perfect combustion and communicates heat relatively slowly at best.

Gas Producers.

Gas producers are the usual adjunct for open-hearth furnaces, excepting where natural gas or blast furnace gas is available. They may be placed far from the furnace, when they deliver cool gas to the regenerators, or close to the furnace, delivering comparatively hot gas to the regenerators, or even be made part of the furnace itself, delivering their hot gas immediately to the ports of the furnace. The latter is undoubtedly the most economical arrangement where practicable.

The following generalizations concerning the relations of the gas producer to the open-hearth furnace may be made: Producers furnish 4,300 to 4,600 cubic meters of gas per metric ton of coal used (150,000 to 160,000 cubic feet per short ton); the gas produced runs 3 to 8 per cent. CO^2, 5 to 20 per cent. H^2. 20 to 30 per cent. CO, and 50 to 60 per cent. N^2; its calorific

power is 750 to 1000 Calories per cubic meter (47 to 63-pound Calories, or 85 to 115 B. T. U. per cubic foot); its calorific power represents 60 to 90 per cent. of the calorific power of the fuel used; in steel-making processes, the keeping of the furnace up to proper heat requires the gasifying of 25 to 35 kilograms (50 to 80 pounds) of coal per hour, in the producers, for each ton of metal capacity of the furnace; good producers gasify 60 to 65 kilograms of coal per hour per each square meter of gas-producing area (10 to 15 pounds per hour per each square foot); a furnace therefore requires some 0.4 to 0.6 square meter (4 to 6.5 square feet) of gas-producing air in the producers for each ton of metal capacity of the furnace.

Flues to Furnace.

In conducting the gases to the furnace, the flues or conduits should be of ample size. If too small the gas must pass through them with high velocity, requiring considerable draft to give them this velocity, which the chimney, or blower may or may not be capable of furnishing. Producers are almost always worked by a steam blower, furnishing mixed air and steam and a plenum of pressure in the upper part of the producer, which suffices to send the gas through the conduits under a slight pressure, and thus avoids any sucking in of air through crevices in the conduits. With too small conduits the resulting friction and high velocity required may give the blower more work than it can do, and thus entail demands for draft upon the furnace stack. A reasonable rule is to give the flues such cross-sectional area that the hot gas which must pass through them shall have a velocity between 2 and 3 meters per second.

Regenerators.

The dimensions of the regenerators are of the first importance to the working of the furnace. They should have sufficient length in the direction the gas currents are passing, so that the gases may be properly cooled or heated; they should have sufficient cross-sectional area of free space, so that the velocity of the gases through them is not too great; they must have sufficient thermal capacity, so that they can absorb the requisite quantity of heat.

Length.—From 4 to 6 meters (13 to 20 feet) is a suitable

length in the direction of the gas currents. This permits the hot products to become properly cooled before going to the chimney, and the gas or air to be properly heated before entering the furnace. The shorter length may be used when the regenerator is of large cross-sectional area, with slow velocity of gas currents through the free spaces; the longer when the regenerator is rather restricted in cross-section and the gas currents have somewhat high velocity.

Cross-Section.—The free-space sectional area should be such that the gases where hottest should not have a calculated velocity of over 3 meters (10 feet) per second, and if calculated for 2 meters (6.5 feet) will give much better results as regards transmission of heat to the checker work. In this manner, knowing how much gas must go through the regenerator and what its maximum temperature will probably be, the cross-section area of free passage space can be calculated. The relation of this to the cross-section of the entire stove must next be considered, and this is entirely a question of how the checker work is built up. If the bricks are stacked close together the free space may be reduced to as much as one-half the total; as ordinarily stacked it may be 60 to 80 per cent. of the total; if perforated bricks are used, as in blast furnace firebrick-stoves, the area of free space averages one-half the total; with ordinary bricks the average is 70 per cent. This is a question which is very variously worked out in different furnaces, and to which not as much scientific thought has been given as should be. The thickness of the bricks influences greatly the relative amount of free space and filled space, and the rate at which the generator heats up or cools off. In a regenerator of given length and cross-section closer packing of the bricks gives more heat absorbing surface, increases the velocity of the gases and diminishes the cross-sectional area of each passage and of the sum of all the passages; some of these factors increase the efficiency of the regenerator, others tend to decrease it, and there are, therefore, several independent variables to be considered in finding the best arrangement for highest efficiency. A numerical solution is indeed a possibility, but is too involved for an elementary presentation of the subject.

Relative Sizes.—The relative sizes of gas and air regenerators is a question of importance which admits of easy solu-

tion by calculation. So far we have treated the pair of regenerators together, and discussed the sum of their cross-sections as deduced from the volume of products passing through at an assumed maximum temperature and allowable velocity. The regenerators at one end of a furnace are, however, usually divided into a pair or set, one for heating gas and the other for heating air. This is not usual where natural gas is used because of the deposition of soot in the regenerator by the latter when it is heated, but nine out of ten open-hearth furnaces preheat their gas as well as the air. The heating capacity of the regenerators should be divided in proportion to the calorific capacities of the gas and air simultaneously heated. The problem is therefore to find the heat capacity per degree of the gas and air used, or, more exactly, the total heat capacity of each of these between the temperature at which they enter the regenerators and that at which it is desired that they should enter the furnace.

Problem 69.

An open-hearth furnace uses producer gas containing, by volume, at it reaches the regenerators:

CO	26.97 per cent.
CO^2	4.37 "
CH^4	0.33 "
H^2	13.00 "
NH^3	0.21 "
H^2S	0.10 "
N^2	54.01 "
Air	1.03 "

Each cubic meter, measured at 20° C. and 720 m. m. barometric pressure, is accompanied by 73.22 grams of moisture, as determined by drawing through a drying tube and weighing the moisture. The air used is at 20° C., 720 m.m. barometer, and three-quarters saturated with moisture. A maximum of 10 per cent. more air is used than is theoretically necessary to completely burn the gas (assuming NH^3 to burn to H^2O and NO^2, and allowing for the air already present in the gas). The gas and air may be both assumed as coming to the regenerators at 20° C., and to be heated in the regenerators to 1200° C.

Required.—(1) The relative volumes of gas and air passing through the gas and air regenerators.

(2) The total amounts of heat necessary to be furnished to each, per cubic meter of gas used.

(3) The relative sizes of the two regenerators.

Solution.—(1) Taking 1 cubic meter of the dry gas, as represented by the analysis, the combustion of its combustible ingredients is represented by the equations:

$$2CO + O^2 = 2CO^2$$
$$CH^4 + 2O^2 = CO^2 + 2H^2O$$
$$2H^2 + O^2 = 2H^2O$$
$$4NH^3 + 7O^2 = 6H^2O + 4NO^2$$
$$2H^2S + 3O^2 = 2H^2O + 2SO^2$$

And since molecules represent volumes, each unit volume of CO, CH^4, H^2, NH^3 and H^2S is seen to require respectively 0.5, 2, 0.5, 1.75, or 1.5 volumes of oxygen. The 1 cubic meter of dry gas therefore requires oxygen as follows:

CO	0.2697×0.5	$= 0.1349$ m³
CH^4	0.0437×2.0	$= 0.0874$ "
H^2	0.1300×0.5	$= 0.0650$ "
NH^3	0.0021×1.75	$= 0.0037$ "
H^2S	0.0010×1.5	$= 0.0015$ "
	Total	$= 0.2925$ "

Air needed	$= 0.2925 \div 0.208$	$= 1.4062$ m³
Add 10 per cent. excess		$= 1.5468$ "
Air present in gas		$= 0.0103$ "
Air to be supplied		$= 1.5365$ "

Each cubic meter of dry gas, at any given conditions of temperature and pressure, would require 1.5365 cubic meters of dry air at the same conditions of temperature and pressure. This, however, is not exactly the relation required, for the reason that the gas is accompanied by considerable moisture, which in reality adds to its volume, while the air is also moist, adding to its volume. Two corrections must therefore be applied; first, to calculate the volume of the moisture accompanying 1 cubic meter of (assumed) dried gas; the second, to calculate the volume of moisture accompanying 1.5365 cubic

meters of (assumed) dry air. Assuming our gas and moist air both at 20° and 720m.m. pressure, the volume of moisture accompanying 1 cubic meter of (assumed) dry gas is the volume of 73.22 grams of moisture at these conditions, which is

$$73.22 \div 1000 \div 0.81 \times \frac{273 + 20}{273} \times \frac{760}{720} = 0.1024 \text{ m}^3$$

The air being 0.75 saturated with moisture at 20°, the tension of this moisture will be $17.4 \times 0.75 = 13$ m.m. The air proper is therefore under 720—13 = 707 m.m. tension instead of 720 m.m. and the volume of the moist air containing 1.5365 cubic meters of (assumed) dry gas is therefore:

$$1.5365 \times \frac{720}{707} = 1.5648 \text{ cubic meters.}$$

The relative volumes of actual (moist) gas and actual (moist) air used are therefore:

$$1.1024 : 1.5684 = 1.0000 : 1.419 \qquad (1)$$

(2) To calculate the heat necessary to raise gas and air from 20° to 1200° per cubic meter of gas used, the best preliminary is to calculate the composition of the gas, *including* its moisture. Since 1 cubic meter of (assumed) dry gas is accompanied by 0.1024 cubic meter of water vapor, the sum being 1.1024 cubic meters, we can calculate the real percentage composition to be:

CO	24.47	per cent.
CO^2	3.96	"
CH^4	0.30	"
H^2	11.79	"
NH^3	0.19	"
H^2S	0.09	"
N^2	48.99	"
Air	0.93	"
H^2O	9.29	"

Of the above quantities the (assumed) dry gas in 1 cubic meter of (actual) moist gas is 0.9071 c.m. The air used for its combustion will therefore be:

$0.9071 \times 1.5365 = 1.3938$ m³ dry air.
$0.9071 \times 1.5648 = 1.4080$ m³ moist air.
$1.4080 - 1.3938 = 0.0142$ m³ of moisture.

The heat required by the 1 cubic meter of (actual) moist gas is found as follows:

Volume × Mean Specific Heat

		20°—1200°
CO	0.2447	
H^2	0.1179	
		× 0.3359 = 0.2895 Calories.
N^2	0.4899	
Air	0.0093	
CO^2	0.0396	× 0.6384 = 0.0253 "
H^2O	0.0929	× 0.5230 = 0.0486 "
CH^4	0.0030	× 0.6484 = 0.0019 "
NH^3	0.0019	× 0.5752 = 0.0011 "
H^2S	0.0009	× 0.5230 = 0.0005 "
		Mean cal. capacity per 1° = 0.3669 "

Total calorific capacity 20°—1200°
$0.3669 \times 1180 = 432.9$ Calories.

The calorific capacity of the moist air simultaneously heated through the same range will be:

Air	1.3938×0.3359	= 0.4682 Calories.
H^2O	0.0142×0.5230	= 0.0074 "
	Sum	= 0.4756 "

Total calorific capacity 20°—1200°
$0.4756 \times 1180 = 561.2$ Calories.

The air regenerator should therefore have $561.2 \div 432.9 = 1.30$ times the heating power or cross-section of the gas regenerator; *i. e.*, 30 per cent. more. Or the combined capacity of the pair of regenerators should be divided so as to give 57 per cent. to the air regenerator and 43 per cent. to the gas regenerator. In ordinary practice it is usual to allow about 60

and 40 per cent. respectively; it is better to calculate ahead for the specific case in hand, if the composition of the gas to be used is known.

Valves and Ports.

No very exact rule can be given as to the size of the gas and air valves, or those leading the products to the chimney. If made too large they are cumbersome to operate and apt to warp; if made too small they give undue obstruction to the flow of gas. A general rule is to calculate the free opening, such as to give the gases passing through a velocity between 3 and 5 meters (10 and 16 feet) per second, allowing, of course, for the average temperature of the gas or air products of combustion passing through them. It may be remarked that while water-seal valves are very convenient, the water is evaporated where in contact with gas or air, and diminishes the heating efficiency of the furnace, the use of a non-volatile oil or a fine sand would appear perferable to water.

The ports are a very important part of the furnace, and may be designed in many different styles for various ways in which a furnace is to be worked. Their cross-section, however, can be calculated when we know the volume of gas or air leaving the regenerators and their temperature, or the volume of the products of combustion entering the regenerators and their temperature. They should be so designed that the velocity of the gases through them is not over 20 meters per second, while 10 meters per second is a better velocity to use. A long furnace can admit of higher velocities at the ports than a short one; but in any case the higher the velocity the farther complete combustion will occur from the ports, and if the velocity is too high for the length of the furnace combustion may even be continued in the opposite regenerators and less than the maximum occur in the furnace. This is a condition to be scrupulously avoided if possible.

Problem 70.

Producer gas of the following composition:

CO	24.47 per cent.	NH^3	0.19 per cent.
CO^2	3.96 "	N^2	48.99 "
CH^4	0.30 "	Air	0.93 "
H^2	11.79 "	H^2O	9.29 "
H^2S	0.09 "		

is burned with 1.408 times its volume of moist air (see Problem 69). The furnace treats 50 metric tons of steel in 12 hours, using 17.5 tons of coal in the producers, from which 15 tons of carbon pass into the gas. The gas and air pass out of the regenerators at 1200°, and the products of combustion (assumed complete) pass into the opposite regenerators at 1400°. Assume a maximum velocity of the hot gas and air as 10 meters per second, as they pass through the ports.

Required.—(1) The volume of gas and air at 20° C. and 720 m.m. barometer used by the furnace per second.

(2) The areas of the gas and air ports.

(3) The velocity of the products entering the opposite ports.

Solution.—(1) The carbon in 1 cubic meter of the gas at standard conditions is

CO	0.2447
CO^2	0.0396
CH^4	0.0030

$$0.2873 \times 0.54 = 0.1551 \text{ kg.}$$

Gas used in 12 hours (standard conditions):

$$15{,}000 \div 0.1551 = 96{,}710 \text{ m}^3$$

Per second = 2.24 m^3

Gas used at 20° C. and 720 m.m.:

$$2.24 \times \frac{273+20}{273} \times \frac{760}{720} = \mathbf{2.53} \text{ m}^3 \text{ per second.} \quad (1)$$

Air used (standard conditions):

$$2.24 \times 1{,}408 = 3.15 \text{ m}^3$$

Air used at 20° C. and 720 m.m.:

$$2.53 \times 1{,}408 = \mathbf{3.56} \text{ m}^3 \text{ per second.} \quad (1)$$

(2) The volume of gas used per minute, as it issues from the ports at 1200°, is

$$2.24 \times \frac{1200+273}{273} \times \frac{760}{720} = 12.8 \text{ m}^3$$

and of air $3.15 \times$ " $\times$ " = 17.9 "

and assuming a maximum velocity for each of 10 meters per second, the areas of the ports must be:

Gas ports	1.28 m^2
Air ports	1.79 "
Sum	3.07 " (2)

(3) There is usually contraction when gases burn, the products having less volume than the gas and air used. Inspecting the equations of combustion of CO, CH^4, H^2, H^2S and NH^3 given in Problem 69, we can construct the following table of relative volumes concerned and the ensuing contraction:

	CO	CH^4	H^2	H^2S	NH^3
Volume used	1.0	1.0	1.0	1.0	1.0
Oxygen used	0.5	2.0	0.5	1.5	1.75
Gases combining	1.5	3.0	1.5	2.5	2.75
Volume of products	1.0	3.0	1.0	2.0	2.5
Contraction	0.5	0.0	0.5	0.5	0.25

Using 1 cubic meter of producer gas the contraction resulting from its combustion with an excess of air is

CO	0.2447×0.5	$= 0.12235$ m^3
CH^4		$= 0.00000$ "
H^2	0.1179×0.5	$= 0.05895$ "
H^2S	0.0009×0.5	$= 0.00045$ "
NH^3	0.0019×0.25	$= 0.00050$ "
Total contraction		$= 0.1822$ "

Since the volume of gas, plus air used, is 2.408 m^3, the volume of the products, at standard conditions, is

$$2.408 - 0.182 = 2.226 \text{ m}^3$$

per cubic meter of gas used under standard conditions. The volume of products per minute, at standard conditions, is, therefore,

$$2.226 \times 2.24 = 4.986 \text{ m}^3.$$

And at 1400° and 720 m.m. pressure:

$$4.986 \times \frac{1400+273}{273} \times \frac{760}{720} = 32.7 \text{ m}^3.$$

Since the sum of the area of gas and air ports is 2.91 m^2, the velocity of the products in these ports will be

$$32.7 \div 3.07 = \mathbf{10.7} \text{ m. per second.} \quad (3)$$

In both the calculations of the size of the ports and the velocity of the products we have assumed the tension of the gas, air or products in the ports to be the prevailing atmospheric tension. This may or may not be exactly true, because the air or gas may be under a slightly less tension, being drawn into the furnace by the stack draft. If the pressure inside the furnace, with doors closed, is greater or less than atmospheric pressure, the tension of the gases in the entrance ports will be correspondingly greater or less than the atmospheric pressure, while the tension of the products will probably always be less than atmospheric pressure, because of the stack draft. Under ordinary conditions these corrections are too small to need to be taken into consideration.

Laboratory of Furnace.

The laboratory consists of the open space enclosed between the hearth, sides, ends and roof. Its dimensions vary with the intended capacity of the furnace and the ideas of the designer. If a hearth is to contain, say, 50 tons of melted steel, which weighs some 7 tons per cubic meter (425 pounds per cubic foot), there will be contained in the furnace at one time 7 cubic meters, or 260 cubic feet of steel. The deeper this lies the more slowly it will be heated or oxidized by the flame, and therefore there is a limiting depth of, say, 50 centimeters, or 20 inches, which it is not advisable to exceed, while a more shallow bath will result in faster working. Assuming a depth of 40 centimeters (16 inches), the volume divided by the depth will give the area of the bath:

$$7 \div 0.4 = 17.5 \text{ square meters}$$
$$260 \div 1.25 = 208 \text{ square feet.}$$

We can then either choose a convenient width, consistent with a practicable roof span, and derive the length, or choose a length and derive the width, or choose a certain ratio of length to width, and derive both. If the width is 3 meters the

length must be 5.8; if the length is assumed 5 meters, the width is 3.5; if the ratio of length to width is 2 to 1, the length figures out 5.92 meters and the width 2.96. These dimensions are those of the bath of metal, and each should be increased by at least 1 meter to get the area of the hearth inside the walls, thus allowing 0.5 meter clear space all around the metal.

If a furnace is short it should be wide and the roof high, in order to give cross-sectional area and thus diminish the velocity of the gases over the hearth. The gases attain their maximum temperature in the laboratory, theoretically, some 1700° to 1900°, and their velocity depends solely on the vertical cross-sectional area of the laboratory or body of the furnace. In Problem 70, for instance, about 5 cubic meters of products of combustion (measured at standard conditions) pass through the furnace per second. At 1800° this volume would be 38 cubic meters, and if the laboratory were 4.5 meters wide by 1.5 meters high above the level of bath, there would be 7.25 square meters of cross-section, and the velocity of the gases would be $38 \div 7.25 = 5.2$ meters per second. This would allow barely 1 second for the hot gases to pass over the bath, which would result in a low rate of heating and probable incomplete combustion, for the gas can only burn as it gets mixed with air, and it is hardly likely that 100 per cent. of it would get mixed with air and consumed in 1 second. Such could only be attained by sub-division of the gas and air and very intimate mixture at the ports. Much of the economy undoubtedly attained by raising the roof of open-hearth furnaces is due to the slowing-up of the gas currents in the laboratory, though it is usually ascribed to avoidance of contact of flame and bath, increased heating by radiation, etc. In the writer's opinion the raising of the roof from 1 to 2 meters, let us say, thus doubling the vertical cross-sectional area, cutting in half the velocity of the gases through the furnace, and doubling the period in which they are able to combine, and to radiate or impart heat to the furnace walls and charge—is the principal reason for the increased economy observed.

An equally important improvement is lengthening the distance between ports. There is a limit to the width of the furnace, set by the practicable arch for the roof; there is also a limit to the height of roof, set by the increasing distance of

the gases from the hearth; when both these factors have reached their maximum, further efficiency of utilization of the heat of combustion can only be secured, as far as the body of the furnace is concerned, by lengthening the hearth. There is no mechanical limit, and in every case the distance between the ports and the velocity of the gases should be such that complete combustion takes place in the furnace laboratory before the products pass into the regenerators.

Problem 71.

H. H. Campbell gives in the *Transactions* of the American Institute of Mining Engineers, 1890, analyses made at the Pennsylvania Steel Co.'s works, as follows:

	Gas Burned, Entering Furnace.	*Products, Leaving Furnace.*
CO^2	5.5 per cent.	3.1 per cent.
O^2	2.3 "	0.7 "
CO	8.2 "	7.1 "
CH^4	7.3 "	0.0 "
H^2	39.8 "	11.6 "
N^2	36.9 "	77.5 "

Required.—(1) The proportion of the calorific power of the fuel developed while passing through the body of the furnace.

(2) The proportion of the air necessary for complete combustion which was used.

Solution.—(1) One cubic meter of the gas contains the following weight of carbon:

$$(0.055+0.082+0.073)\times 0.54 = 0.1134 \text{ kg.}$$

One cubic meter of products contains:

$$(0.071+0.031)\times 0.54 = 0.0551 \text{ kg.}$$

Therefore, volume of products per 1 cubic meter of gas:

$$0.1134 \div 0.0551 = 2.06 \text{ m}^3.$$

Calorific power of 1 cubic meter of gas:

CO	$0.082\times 3062 =$	251 Calories
CH^4	$0.073\times 8623 =$	629 "
H^2	$0.398\times 2613 =$	1040 "
		1920 "

Calorific power of 2.06 cubic meters of products:

CO	$0.071 \times 3062 =$	217 Calories.
H^2	$0.116 \times 2613 =$	303 "
		520 "
	$520 \times 2.06 =$	1071 "

Heat developed in the furnace:

$$1920 - 1071 = 849 \text{ Calories.}$$

Proportion of the possible heat development:

$$849 \div 1920 = 0.442 = \mathbf{44.2} \text{ per cent.} \qquad (1)$$

(2) The 1 cubic meter of gas needed, to burn its combustible constituents, the following amount of oxygen:

CO	0.082×0.5	$= 0.041$ m³
CH^4	0.073×2.0	$= 0.146$ "
H^2	0.98×0.5	$= 0.199$ "
	Sum	$= 0.386$ "
Oxygen present in gas		$= 0.023$ "
Oxygen needed from air		$= 0.363$ "
Air $= 0.363 \div 0.208$		$= 0.745$ "

The 2.06 m³ of products of incomplete combustion require for their combustion:

CO	$0.071 \times 2.06 \times 0.5 =$	0.0731 m³ oxygen.
H^2	$0.116 \times 2.06 \times 0.5 =$	0.1195 " "
	Sum =	0.1926 " "
Oxygen present in the products	=	0.0070 "
Oxygen needed from the air	=	0.1856 "
Air needed to complete combustion	=	0.892 "
Total air needed for complete combustion	=	1.745 "
Air supplied in the furnace	=	0.853 "

Percentage supplied:

$$0.853 \div 1.745 = 0.489 = \mathbf{48.9} \text{ per cent.} \qquad (2)$$

It is almost needless to remark that with less than half the air necessary for complete combustion supplied, a high calorific intensity of flame and a high utilization of the calorific power of the fuel are impossible. More air should have been used and the furnace made longer, so as to secure perfect combustion in the furnace, and not have over half the possible development left to take place in the regenerators or stack.

Chimney Flues and Chimney.

The gases pass into the chimney flues at from 150° to 450°. If their volume at an assumed average temperature of, say, 300° is calculated, they can be given an assumed velocity of 2 to 3 meters (5 to 10 feet) per second, and thus a suitable cross-sectional area of the chimney flues obtained. The stack will work best with a velocity of 5 meters per second, and thus its cross-sectional area may be calculated. A height of 25 to 30 meters (75 to 100 feet) is sufficient for most furnaces.

Miscellaneous.

Some other data useful in figuring up the dimensions and running conditions of modern open-hearth steel furnaces are the following, taken mostly from an article by H. D. Hess, in the *Proceedings* Engineering Club of Philadelphia, January, 1904:

Average coal consumption, in pounds, per hour per ton of metal capacity of the furnace, 55 to 80.

Cubical feet of space in one pair of regenerators, per ton of metal capacity of the furnace, 30 to 75.

Cubic feet of space in one pair of regenerators per pound of coal consumed per hour, 0.5 to 1.0.

A correllation and combination of data of this sort, with details as to the actual working of the furnaces, would point the way towards a general solution, which would furnish the best condition for every possible case, with strict consideration for all the variables involved.

CHAPTER XI.

THERMAL EFFICIENCY OF OPEN-HEARTH FURNACES.

The ordinary open-hearth steel furnace receives cold pig iron, cold scrap, warm ferro-manganese, cold limestone and cold ore, it receives cold air and moderately warm producer gas, and it furnishes melted steel and slag at the tapping heat. The larger part of the usefully applied heat is that contained in the melted steel, for it must be melted in order to be cast, and when once taken away from the furnace the latter is done with it.

The total heat available for the purposes of the furnace and which should be charged against it consists of the following items:

(1) Heat in warm or hot charges.
(2) Heat in warm or hot gas as it reaches the furnace.
(3) Heat in warm or hot air as it reaches the furnace.
(4) Heat which could be generated by complete combustion of the gas.
(5) Heat of oxidation of those constituents of the charge which are oxidized in the furnace.
(6) Heat of formation of the slag.

The items of distribution of this total will be as follows:

(1) Heat in the melted steel at tapping.
(2) Heat absorbed in reducing iron from iron ore.
(3) Heat absorbed in decomposing limestone added for flux.
(4) Heat absorbed in evaporating any moisture in the charges.

These first three items constitute the usefully applied heat, and their sum measures the net thermal efficiency of the furnace.

(5) Heat absorbed in reducing ferric oxide to ferrous oxide.
(6) Heat in the slag.
(7) Heat lost by imperfect combustion.

(8) Heat in the chimney gases as they leave the furnace.
(9) Heat absorbed by cooling water.
(10) Heat lost by conduction to the ground.
(11) Heat lost by conduction to the air.
(12) Heat lost by radiation.

(1) Heat in Warm Charges.

If the pig iron is charged melted instead of cold an immense amount of thermal work is spared the furnace, and it should be charged with all the heat (reckoning from 0° C. as a base line) which is in the melted pig iron as it runs into the furnace. This will average 275 Calories per unit of pig iron, but should be actually determined calorimetrically in each specific instance wherever possible. The net thermal efficiency of the furnace will figure out higher with cold charges than with melted pig iron, because, with a possible flame temperature of 1,900° C. in the furnace, heat is absorbed much more rapidly by cold charges than by hot ones, and a larger percentage of the available heat will be thus usefully applied.

Scrap is almost always charged cold, but if any of it is hot its weight and temperature should be known and the amount of heat thus brought in charged against the furnace. Or a small piece may be dropped into a calorimeter and its heat content per unit of weight measured directly, and thus the heat in all the hot scrap used may be estimated.

Ferro-manganese is often added cold, but usually is preheated to cherry redness (about 900°) in another small furnace, in order that it may dissolve more quickly in the bath. Knowing its weight, temperature and specific heat, the heat which it brings into the furnace can be calculated; a better plan is to drop a piece into a calorimeter and measure the actual heat in a sample of it.

Limestone and ore are almost invariably put into the furnace cold. If used warm the heat in them can be determined by the methods just described.

(2) Heat in the Gas Used.

By this is meant, not the heat in the gas after it is heated by the regenerators, but its sensible heat as it reaches the furnace. This applies only to furnaces where the producers

or gas supply are independent of the furnace. Where the producers are an integral part of the furnace it is impracticable to consider them separately from the furnace, and the efficiency of the whole plant, including the producers, must be considered together. But where the gas supply from whatever source comes to the furnace from outside, and reaches the furnace warm, its sensible heat is to be charged against the furnace as part of the heat which the furnace must account for. If the gas comes from producers its amount is satisfactorily found from the known weight of carbon gasified per hour, or per furnace charge, and the weight of carbon contained in unit volume of gas, as calculated from its analysis. If gas comes from a common main which supplies several furnaces, or is simply natural gas, its amount can only be roughly estimated by measuring the area of the gas supply pipe or flue and measuring the velocity of flow by a pressure gauge or Pitot tube or anemometer. None of these methods just mentioned are satisfactorily accurate, and there is great need of simple methods for determining accurately the flow of gases in flues or pipes. If the velocity of warm gas is determined suitable correction for its temperature must be made to reduce it to volume at standard conditions.

(3) Heat in the Air Used.

If the air coming to the furnace is warm its sensible heat must be charged against the furnace. If the air is warmed, however, before it goes into the regenerators by waste heat from the furnace itself, then its sensible heat should *not* be charged against the furnace, because that would amount to charging the furnace twice with this quantity of heat. Such preheating it in reality only a part of the regenerative principle, even though it may not be done in regenerators, but, for instance, by circulating air around a slag-pot or through the hollow walls of the furnace. If the air used is moist its moisture should not be omitted in the calculation.

The amount of air used is best determined by a comparison of the analyses of gas and chimney products, and a calculation based on the carbon contents of each and the known volume of gas used.

(4) Heat of Combustion.

Under this head comes the principal item of heat available for the furnace. In reckoning it we should calculate the total heat which could be generated by the perfect combustion of the gas used, to CO^2, N^2 and H^2O vapor. If there is in reality imperfect combustion, as is shown by analysis of the chimney gases, that is a defect of operation of the furnace which should be written down against it. Problem 71 showed an actual case in which there was very incomplete combustion in the body of the furnace, but where combustion was afterwards completed in the regenerators. In such a case the same principle applies; the furnace must be charged with the total calorific power of the fuel used, and incomplete combustion can be charged against the furnace as a whole only on the basis of unconsumed ingredients in the chimney gases—the products finally rejected by the furnace. If there is poor combustion in the body of the furnace and combustion is only completed in the regenerators, the furnace will not give as high net thermal efficiency as if combustion were complete above the hearth.

(5) Oxidation of the Bath.

The oxidation of carbon, iron, silicon, manganese and sometimes phosphorus and sulphur, add a not inconsiderable amount to the heat resources of the furnace. Carbon should be burnt to CO^2, iron is usually oxidized to FeO, manganese to MnO, silicon to SiO^2, phosphorus to P^2O^5, and sulphur to SO^2. All of these oxidations generate heat, and, moreover, heat which should be very efficiently utilized, being produced in direct contact with the metallic bath; it should all be charged against the furnace as part of its available heat.

(6) Formation of Slag.

The metallic oxides produced unite with each other, and with the lime and silica of ore used and lining of the hearth to produce the slag, the heat of formation of which can be calculated and counted in as available heat.

(1) Heat in Melted Steel.

This is a large item in the work done by the furnace; in fact, usually the largest single item. It should be determined

calorimetrically when possible; if this is not done its temperature should be known and its composition, in order to compare it with the calorimetric experiments of others, and thus derive a probable value for its heat contents. Not many experimental values in this line have so far been published, and a very much needed investigation is one upon the total heat in melted steels of different compositions at different temperatures. Values from 275 to 350 Calories per kilogram have been observed.

(2) Heat of Reduction of Iron from Ore.

This is an item which appears whenever ore is used to facilitate oxidation of the bath. The weight and composition of the charges and the products will easily show how much iron has been reduced. The ore used is almost always hematite, less frequently magnetite; hydrated iron oxides are not used for obvious reasons. The heat absorbed is 1,746 Calories per kilogram of iron reduced from Fe^2O^3 and 1,612 Calories per kilogram from Fe^3O^4.

(3) Decomposition of Limestone Flux.

If limestone is charged raw, as is usually done in order to avoid the dusting caused by using burnt lime, then the furnace is called upon to burn this limestone in place of the lime kiln. The heat absorbed may be taken as either

451 Calories per kilogram of $CaCO^3$ decomposed.
1,026 Calories per kilogram of CO^2 driven off.
806 Calories per kilogram of CaO produced.

(4) Evaporation of Moisture in the Charges.

If the ore, flux, scrap or ore are put into the furnace wet their moisture must be evaporated. The correct figure for this evaporation is the latent heat at ordinary temperatures, viz.: 606.5 Calories per kilogram. This allows for the heat required to convert into cold vapor of water, and puts the H^2O thereafter upon the same basis as all the other gas going out of the furnace. The chimney gases carry out sensible heat, and the H^2O in them can be calculated as carrying out a certain amount of heat as gas, reckoning from zero, and thus the correct chimney loss obtained. It is incorrect either to

charge the latent heat of vaporization as chimney loss or to charge the sensible heat of the water vapor in the chimney gases to heat absorbed in evaporating water in the furnace. It is also incorrect to do as is frequently done, viz.: to calculate the heat required to evaporate the moisture to water vapor at 100°—637 Calories—and say that this is the heat to evaporate the moisture. With almost no moisture in the gases, the moisture of the charges would commence to evaporate at once, while they were yet cold, and the moisture is no more evaporated at 100° or to vapor at 100° than it is to 200° or 500°. The only safe course is to confine the evaporation heat to that necessary to convert the moisture into cold vapor, and let its sensible heat as it escapes as vapor at any other temperature be reckoned in with the sensible heat of the chimney gases.

(5) Reduction of Ore Into the Slag.

While considerable of the iron in the ore used is reduced to the metallic state, yet often the larger part is reduced merely to the state of FeO, and as such goes into the slag. The amount so reduced can be determined by subtracting the iron reduced from ore from the total iron in the ore used; the differences gives the iron from the ore going into the slag as FeO. The weight of FeO corresponding is then easily calculated. The heat absorbed in this partial reduction is:

446 Calories per kilogram of FeO reduced from Fe^2O^3.

341 Calories per kilogram of FeO reduced from Fe^3O^4.

(6) Heat in Slag.

This is usually a small item in open-hearth practice, but may amount to a very considerable one in the method of running with large ore charges, as in the Monell process. The variations of composition of the slag, and especially in the temperature at which it is run off, are so large that the heat in the slag should always be determined calorimetrically for each specific case. If assumptions have to be made, 450 to 550 Calories per kilogram of slag would be assumed. The weight of slag is seldom taken, although it could in most cases be done if desired. If the weight is not known it may be calculated from the known weight of either iron, manganese or

phosphorous going into it, as seen from the balance sheet and the percentages of these elements in the slag as shown by analysis.

(7) Loss by Imperfect Combustion.

This is based upon the unconsumed ingredients of the chimney gases, as shown in an analysis. From this the calorific power of the unburnt gases in 1 cubic meter can be calculated. If then we know the volume of chimney gases per unit of charge, we get the heat loss by imperfect combustion per unit of charge. The volume of chimney gas is found by means of the carbon in it, which must all come from the carbon in the gas used, plus the carbon oxidized out of the charges, plus the carbon of CO^2, driven off raw limestone used as flux. Or, putting it in another way, the total carbon going into the furnace in any form, less the carbon in finished steel, must give the carbon in the chimney gases. This divided by the weight of carbon in unit volume of chimney gas gives the volume of the latter, per whatever unit of charge is used as the basis of calculations. This volume times the calorific power of unit volume of chimney gas, gives the total heat lost by imperfect combustion.

(8) Sensible Heat of Chimney Gases.

The temperature of these gases should be taken as they enter the chimney flue. Their amount is determined as explained under the previous heading. The water vapor contained should not be overlooked, being reckoned simply as vapor or gas in exactly the same category as the other gases. The analysis of the chimney gases being usually given on dried gas, a separate determination of the moisture carried per unit volume of such dried gas is necessary. If this is not done an approximation can be made by considering all the hydrogen in the gas burned to form water vapor, and add in the moisture of the air used and the moisture in the charge.

(9) Heat Lost in Cooling Water.

This is a very variable amount, and must be determined for each furnace by measuring the amount of water used per unit of time and its temperature before reaching and after leaving

the furnace. Doors are frequently water-cooled, also ports, where the heat is fiercest, and sometimes a ring around the hearth at the slag line.

(10) Loss by Conduction to the Ground.

This is a quantity extremely difficult to measure or to estimate. If a closed vessel filled with water were put into the foundations the rate at which its temperature rose might give some idea of the rate at which heat passed in that direction per unit of surface contact. At present, lacking all reliable data, we must put this item in the " by difference " class.

(11) Loss by Conduction to the Air.

This is an amount which can be observed and calculated with some approach to satisfaction. The *sina qua non* for this parpose is a Féry radiation pyrometer, by which the temperature of the outside of the furnace at different parts can be accurately determined. Then the velocity of the air blowing against the furnace, if it is in a current of air, is observed with a wind gauge, and its temperature before reaching the furnace. With these data and by the methods of calculation before explained in these calculations (Part I, Chap. VIII) the heat lost to the air may be calculated.

(12) Radiation Loss.

Having determined the temperature of the outer surface of the furnace and measured its extent, as above explained, the radiation loss can also be calculated, knowing the mean temperature of the surroundings, by the principles of radiation, having due regard to the nature of the radiating surface. Tables of specific radiation capacity of different substances (fire-brick, stone, iron) will be found at the reference just given above.

Problem 72.

Jüptner and Toldt (Generatoren und Martinöfen, p. 73) observed the following data with regard to an open-hearth steel furnace charge:

Weight of cold charges, at 26° C.....	3,745 kg.
Weight of hot charges, at 700° C.....	1,700 "
Total weight of charge.....	5,445 "

Average composition of charge	C =	1.07 per cent.
	Si =	0.50 "
	Mn =	1.33 "
Coal gasified in producers		1,980 kg.
Carbon gasified from coal		47.13 per cent.
Average composition of dried gas used	CO^2	3.81 "
	O^2	0.98 "
	CO	23.82 "
	CH^4	0.42 "
	H^2	8.75 "
	N^2	62.22 "
Moisture accompanying each m^3 of gas	=	82 grams.
Temperature of gas reaching furnace		165° C.
Temperature of air used		26° C
Moisture accompanying each m^3 of air		12 grams.
Barometer		717 m.m.
Steel produced		5,191 kg.
Composition of steel	C =	0.12 per cent.
	Si =	0.04 "
	Mn =	0.19 "
Temperature of steel when tapped		1410° C.
Heat in 1 kg. steel, by calorimeter (to 0° C.)		277 Cal.
Composition of slag	SiO^2	45.65 per cent.
	FeO	33.60 "
	MnO	18.21 "
	CaO	2.54 "
Weight of slag		425 kg.
Temperature of slag when issuing		1,410° C.
Heat in 1 kg. slag, by calorimeter (to 0°)		560 Cal.
Composition of the stack gases (dry)	CO^2	11.12 per cent.
	O^2	6.78 "
	N^2	82.10 "
Temperature of the gases in chimney flue		500° C.

Requirements:

(1) A balance sheet of materials entering and leaving the furnace.

(2) A balance sheet of the heat available and its distribution.

(3) What excess of air above what is necessary for complete combustion is used, and what per cent. of all the available heat of the furnace is thereby lost?

(4) What is the thermal efficiency of the furnace?

Solution: (1)

BALANCE SHEET OF MATERIALS.

Charges.		*Steel.*	*Slag.*	*Gases.*
Metal,	**5,445** kg.			
C,	58 "	6	...	52
Si,	27 "	2	25	....
Mn,	72 "	10	62	....
Fe,	5,288 "	5,173	115	....
Limestone,	**20** "			
CaO,	11 "	....	11	....
C,	2.5 "	....	....	2.5
O,	6.5 "	....	....	6.5
Hearth,				
SiO^2	132 "	....	132	....
Gas,	**7,884** "			
C,	933 "	....	....	933
O,	2,003 "	....	....	2,003
H,	118 "	....	....	118
N,	4,830 "	....	....	4,830
Air,	**16,026** "			
O,	3,812 "	....	80	3,732
N,	12,195 "	....	....	12,195
H,	19 "	....	....	17
Totals,	29,507 "	5,191	425	23,891

NOTES ON THE BALANCE SHEET.

The distribution of carbon, silicon, manganese and iron is governed by the known amounts of these elements present in the steel, the rest of the carbon going into the gases (as CO^2), and the manganese, silicon and iron passing into the slag (as MnO, SiO^2 and FeO, respectively.)

The amount of limestone used was not stated, but was deduced from the fact that the slag was said to weight 425 kilos. and to contain 2.54 per cent. of CaO, which makes the CaO 11 kilos. and assuming pure limestone, this would bring in 9 kilos. of CO^2, which appears on the balance sheet as 2.5 kilos. of carbon and 6.5 kilos. of oxygen, contributed to the gases.

The weight of silica contributed by the hearth is deduced from the fact that the slag must contain the silicon, manganese and iron oxidized from the charge, as SiO^2, MnO and FeO,the CaO of the flux and the SiO^2 contributed by the hearth, and its total weight is 425 kilos. The ingredients of the slag must, therefore, be

		Kg.
SiO^2	$25 \times 60/28 =$	53.5
MnO	$62 \times 71/55 =$	80.0
FeO	$115 \times 72/56 =$	147.9
CaO	$=$	11.0
	Sum	293
From hearth (difference)		132
Total slag		425

The gas used we find by starting with the fact that 1,980 kilos. of coal is used, from which 47.13 per cent, of carbon enters the gases. This makes carbon in the gases 933 kilos. Each cubic meter of dry gas, as analyzed, contains 0.2805 cubic meter of CO^2, CO and CH^4 added together, and therefore, $0.2805 \times 0.54 = 0.1515$ kilos. of carbon. The volume of dry producer gas used is therefore, at standard conditions, $933 \div 0.1515 = 6{,}160$ cubic meters, containing by its analysis:

CO^2	$6{,}160 \times 0.0381 =$	235 m^3 =	465 kg.
O^2	" $\times 0.0098 =$	60 m^3 =	86 "
CO	" $\times 0.2382 =$	1,467 m^3 =	1,840 "
CH^4	" $\times 0.0042 =$	26 m^3 =	19 "
H^2	" $\times 0.0875 =$	539 m^3 =	49 "
N^2	" $\times 0.6222 =$	3,833 m^3 =	4,830 "
		6,160 m^3 =	7,297 "

The moisture is 82 grams per each cubic meter of gas, measured at 26° and 717 m.m. pressure; but the 6,160 cubic meters of gas at standard conditions would be 7,175 cubic meters at those conditions of temperature and pressure, and therefore be accompanied by

$$7{,}175 \times 82 = 588{,}350 \text{ grams}$$
$$= 588 \text{ kg. of } H^2O \text{ vapor.}$$

We can now enter the gas on the balance sheet either as so much CO^2, CO, H^2O, etc., or else resolve it into its essential constituents C, H, O and N, which course we have followed on the balance sheet. The carbon in the gas, is 933 kg. by assumption, the oxygen is 8/11 the CO^2, all the O^2, 4/7 the CO and 8/9 the H^2O, a total amounting to 2,003 kilos; the hydrogen is 4/16 the CH^4, all the H^2 and 1/9 the H^2O, a total of 118 kilos.

The air supplied is best found from the volume of the chimney gases. The total carbon entering these is $52+2.5+933 = 987.5$ kilos., as seen from the balance sheet. Each cubic meter of dry chimney gas contains 0.1112 m^3 of CO^2, carrying $0.1112 \times 0.54 = 0.0600$ kilos. of carbon. The volume of dry chimney gas at standard conditions is therefore $987.5 \div 0.0600 = 16{,}458$ m^3. This contains $16{,}458 \times 0.8210 = 13{,}512$ m^3 of N^2, and since 3,833 cubic meters came in with the gas 9,679 m^3 must have come in with the air, corresponding to 12,220 m^3 of dry air at standard conditions. This would consist of 12,195 kilos. of N^2 and 3,660 kilos. of O^2. To find the moisture present the volume of this air at 26° and 717 m.m. pressure would be 14,230 m^3, and would be therefore accompanied by

$$14{,}230 \times 12 = 170{,}760 \text{ grams} = 171 \text{ kg. of } H^2O.$$

This consists of 19 kilos. of hydrogen and 152 kilos. of oxygen, the latter increasing the total oxygen in the air used to $3\,660+152 = 3{,}812$ kilos.

(2) Heat Balance Sheet.

Heat Available.

	Cal.	*Per-centages.*
Heat in the warm charges	189,210	= 2.45
Sensible heat of air used	99,480	= 1.29
Sensible heat of gas used	360,550	= 4.68
Heat of combustion of gas	6,202,300	= 80.44
Heat of oxidation of the bath	833,600	= 10.81
Heat of formation of slag	24,200	= 0.31
Total	7,709,340	= 100.00

Heat Distribution.

In melted steel at tapping.....	1,437,900 =	18.65
Decomposition of limestone.....	9,200 =	0.12
Sensible heat of slag.....	238,000 =	3.09
Sensible heat of chimney gases.....	3,118,450 =	40.45
All other losses, not classified.....	2,905,790 =	37.69
Total.....	7,709,340 =	100.00

Notes on the Heat Balance Sheet.

The warmed charges weighed 1,700 kilos. at 700°, and the cold charges 3,745 kilos at 26°. Taking 0° C. as the base line the sensible heat in these is

	Cal.
$1,700 \times 0.15 \times 700$ =	178,500
$3,745 \times 0.11 \times 26$ =	10,710
Sum =	189,210

The air used contains, at standard conditions, 12,220 m^3 of air and $171 \div 0.81 = 211$ m^3 of water vapor. These carry at 26°, heat as follows:

	Cal.
$12,220 \times 0.3037 \times 26$ =	98,490
$211 \times 0.3439 \times 26$ =	990
Sum =	99,480

The gas used, coming in at 165° C., carries in heat as follows:

		Cal.
O^2, CO, H^2, N^2	5,899 $m^3 \times 0.3075$ =	1,814
CO^2	235 $m^3 \times 0.4063$ =	95
CH^4	26 $m^3 \times 0.4163$ =	11
H^2O	726 $m^3 \times 0.3648$ =	265
Average calorific capacity per 1° =		2,185
Heat content $2,185 \times 165$ =		360,525

The heat of combustion is that of the combustible ingredients of the gas used to CO^2 and H^2O vapor:

		Cal.
CO	1,467 $m^3 \times 3{,}062$	= 4,492,000
CH^4	26 $m^3 \times 8{,}598$	= 223,500
H^2	539 $m^3 \times 2{,}613$	= 1 486,800
	Sum	= 6,202,300

The heat of oxidation of the bath is from the various substances oxidized:

		Cal.
C to CO^2	$52 \times 8{,}100$	= 421,200
Si to SiO^2	$25 \times 7{,}000$	= 175,000
Mn to MnO	$62 \times 1{,}653$	= 102,500
Fe to FeO	$115 \times 1{,}173$	= 134,900
	Sum	= 833,600

The heat of formation of the slag is the heat of combination of 80 kilos. of MnO, 148 kilos. of FeO and 11 kilos. of CaO, with 186 kilos. of SiO^2. This will be, since the bases are largely in excess of the silica:

$$186 \times 130 = 24{,}200 \text{ Cal.}$$

The figure 130 is an average for the heat of combination of 1 kilo. of SiO^2 with about 2 parts of FeO to 1 part MnO.

The heat in the steel at tapping is simply its weight multiplied by its heat contents per kilo. $(5{,}191 \times 277)$.

The heat in the slag is similarly obtained (425×560).

The decomposition of limestone represents 9 kilos. of CO^2 liberated, and the heat absorbed is $9 \times 1{,}026$.

The sensible heat in the chimney gases is obtained by first noting that their volume (measured dry), as already obtained, is 16,458 cubic meters. The CO^2, 11.12 per cent., becomes, therefore, 1,843 m^3; the O^2, 1,116 m^3; N^2, 13,512 m^3, while the H^2O accompanying this will be 9 times the weight of hydrogen passing into the gases, which is $9 \times (118+17) = 1{,}215$ kilos. $= 1{,}500$ m^3. A simpler way to get the volume of the water vapor is to observe that it is always equal to the volume of hydrogen going into it, and, therefore, in this case would be $(118+17) \div 0.09 = 1{,}500$ m^3. The heat carried out by these gases would therefore be:

N^2+O^2 = 14,628 $m^3 \times 0.3165$ = 4629.8 Cal. per 1°
CO^2 = 1,843 $m^3 \times 0.4800$ = 984.4 " "
H^2O = 1,500 $m^3 \times 0.4150$ = 622.5 " "

Calorific capacity = 6236.9 " "
Total capacity = 3,118,450 " per 500°

The heat balance sheet as a whole discloses the fact that in this furnace the fuel only supplies some 80.5 per cent. of the total heat available, and that about 10.8 per cent. is furnished by the oxidation of the bath itself. On the other hand, the melted steel accounts for 18.6 per cent., while chemical reactions absorb almost none, giving a net thermal efficiency of slightly under 19 per cent. The other important items are 40.5 per cent. of the total heat lost up the chimney, and 38 per cent. lost by radiation and conduction. Such data as these point the way to avenues of possible saving or avoidance of waste of heat.

(3) The excess of air is obtained directly from the chimney gases. The 1,116 m^3 of oxygen, unused, represents $1{,}116 \div 20.8$ = 5,365 m^3 of air in excess, which leaves 16,458—5,365 = 11,093 m^3 of air which came in and was used. The percentage of air used in excess of that which was necessary was:

$$5{,}365 \div 11{,}093 = 0.4845 = \mathbf{48.5} \text{ per cent.} \qquad (3)$$

No properly run open-hearth regenerative gas furnace should ever have such a large excess of air, for it cuts down the temperature of the flame and leads to high chimney losses.

The air used brought in 171 kilos of water vapor, and therefore the excess air brought in

$$171 \times \frac{48.5}{148.5} = 56 \text{ kilos. of water,}$$

the volume of which, at standard conditions, would be

$$56 \div 0.81 = 61 \text{ cubic meters.}$$

The excess air, with its accompanying water, going into the chimney at 500°, carried out heat as follows:

	Cal.
$5{,}365 \times 0.3165 \times 500$ =	849,000
$61 \times 0.4150 \times 500$ =	12,650
	861,650

Representing 861,650 ÷ 7,709,340 = 0.112 = **11.2** per cent. (3)

(4) The thermal efficiency has been already added up as

18.65 + 0.12 = **18.77** per cent. (4)

Problem 73.

In the open-hearth furnace of the preceding problem, assume that the calculations therein made showed that, per heat of steel produced, 5,191 kilograms, there entered and left the furnace the following volumes of gases, measured at standard conditions:

	Producer Gas.	*Air.*	*Chimney Gases.*
CO^2	235 m^3	.....	1,830 m^3
O^2	60 m^3	3,833 m^3	1,116 m^3
CO	1,467 m^3	.....	.....
CH^4	26 m^3	.....	.....
H^2	539 m^3	.....	.....
N^2	3,834 m^3	9,679 m^3	13,512 m^3
H^2O	726 m^3	211 m^3	1,500 m^3

The temperature of air used was 26°, of producer gas 165°, of chimney gases 400°. The excess of air used was 48.5 per cent. The gas and air entered the laboratory of the furnace preheated to 1,100°, and the products of combustion entered the regenerators at 1,450. Items of heat balance sheet:

Available.

	Calories
In warm charges	189,210
Sensible heat of air used at 26°	90,480
Sensible heat of gas used at 165°	360,550
Heat of combustion of the gas	6,202,300
Heat of oxidation of the bath	833,600
Heat of formation of slag	24,200
	7,700,340

Distribution.

In melted steel at tapping at 1,410°	1,437,900
In slag at tapping at 1,410°	238,000
Decomposition of limestone	9,200
Sensible heat in chimney gases at 400°	3,065,350
All other losses, not classified	2,949,890
	7,700,340

Required:

(1) The thermal efficiency of the regenerators.

(2) The thermal efficiency of the laboratory of the furnace.

(3) The temperature of the flame.

(4) The change in (3) if only the theoretical amount of air for combustion were used.

Solution:

(1) The products of combustion, entering the regenerators at 1,450°, carry into them the following amounts of heat:

		Calories.
CO^2	$1,830 \times 0.689$	= 1,261
$O^2 + N^2$	$14,628 \times 0.342$	= 5,003
H^2O	$1,500 \times 0.557$	= 836
Calorific capacity per 1°		= 7,100

Calorific capacity per 1,450° = 10,295,000 Calories.

The same gases entering the chimney flue at 400° carry with them the following amounts:

		Calories.
CO^2	$1,830 \times 0.458$	= 838.1
$O^2 + N^2$	$14,628 \times 0.314$	= 4,593.2
H^2O	$1,500 \times 0.400$	= 600.0
Calorific capacity per 1°		= 6,031.3

Calorific capacity per 400° = 2,412,500 Calories.

The gas used for combustion, entering the regenerators at 165° and leaving it at 1,100°, carried into the regenerators 360,550 Calories, as already given in the balance sheet, and carried out at 1,100° the following:

		Calories.
CO^2	235×0.612	= 143.8
CH^4	26×0.620	= 16.1
O^2, N^2, H^2, CO	$5,899 \times 0.333$	= 1,964.4
H^2O	726×0.505	= 366.6
Calorific capacity per 1°		= 2,490.9

Calorific capacity per 1,100° = 2,780,000 Calories.

Heat abstracted from regenerators:

2,780,000—360,550 = 2,419,450 Calories.

The air used, entering the regenerators at 26°, carries in as sensible heat 90,480 Calories, as already given in the balance sheet, and issuing from them at 1,100° carries out the following:

	Calories.
O^2+N^2	$13,512\times0.333 = 4,499.5$
H^2O	$211\times0.405 = 85.5$
Calorific capacity per 1°	$= 4,585.0$

Calorific capacity per 1,100° = 5,043,500 Calories.

Heat abstracted from regenerators:

5,043,500—90,500 = 4,953,000 Calories.

The thermal efficiency of the regenerators may now be calculated from three standpoints. There is no doubt that the gas and air take from the regenerators, and return to the body of the furnace 2,419,450 + 4,953,000 = 7,372,450 Calories. This is, therefore, the usefully returned heat, and the ratio of this to the heat received by the regenerators measures their efficiency *qua* regenerators. The three figures obtained for this efficiency depend on what is to be considered as the heat chargeable against the regenerators. Are they to be charged with all the heat in the hot products at 1,450° (10,295,000 Calories), or only with the heat left in the regenerators by these products leaving at 400° (10,295,000—2,412,500 = 7,882,500 Calories), or perhaps only with the heat carried in less a certain assumed amount representing the minimum temperature to which it is desirable to cool the products before they enter the chimney?

If we charge the regenerators with all the heat *brought in* by the products their thermal efficiency figures out:

$$\frac{7,372,750}{10,295,000} = 0.72 = \mathbf{72} \text{ per cent.} \qquad (1)$$

If we charge them with the heat *left in* the regenerators, by the products, their efficiency is:

$$\frac{7,372,450}{7,882,500} = 0.94 = \mathbf{94} \text{ per cent.} \qquad (1)$$

leaving 7 per cent. of the heat chargeable against them lost by radiation from their walls and conduction to the ground.

If we think that the first calculation gives too low an efficiency, because the gases must leave the regenerators hot, in order to be used for chimney draft, and therefore some or all of the heat in the chimney gases should not be charged against the regenerators, on the other hand, the second calculation may represent too high an efficiency, because the gases may be discarded to the chimney at a higher temperature than is necessary to provide the requisite chimney draft, and this *excess of* chimney temperature and consequent heat loss is a defect of the regenerators which they should be charged with. If we assume that a chimney gives very nearly its maximum drawing capacity with the gases entering it at 300°, it would be perfectly proper to charge the regenerators with all the heat which could be given out by the products in cooling from 1,450° to 300°, heat which they should have entirely absorbed. In the case in hand, the products at 300° would contain (by calculations similar to those already made) 1,777,400 Calories, leaving 10,295,000—1,777,400 = 8,517,600 Calories chargeable against the regenerators, as the heat which they should have absorbed or intercepted. Measured by this standard, their efficiency is:

$$\frac{7,372,450}{8,517,600} = 0.87 = \mathbf{87} \text{ per cent.} \qquad (1)$$

The losses from the regenerators in this view would be 7 per cent. (about) by radiation and 7 per cent. by *unnecessary* chimney loss.

Comparing these three methods of considering efficiency, the third appears to the writer as the fairest, and the one which gives the metallurgist the most reliable criterion of the real work which his regenerators are doing for him, and the best basis of comparison when considering the work of different regenerators or of the same regenerators under different conditions.

(2) The laboratory of the furnace, the space enclosed between the hearth, roof, side walls and ports, receives from the entering preheated gas and air their sensible heat, and the heat generated by combustion. In the case in point these items total, as already calculated:

	Calories.
Sensible heat in preheated gas.....	2,722,300
Sensible heat in preheated air.....	5,043,500
Heat generated by the combustion.....	6,202,300
Total.....	13,968,100
Hot products at 1,450° take out.....	10,295,000
Heat left in the laboratory.....	3,673,100

These figures show that the laboratory of the furnace appropriates to its own purposes 3,673,100 Calories out of the 13,968,100 Calories poured into it. This part of the furnace, therefore, *qua* laboratory, has an efficiency in this respect of

$$\frac{3,673,100}{13,968,100} = 0.26 = \mathbf{26} \text{ per cent.} \qquad (2)$$

This is the datum which would be useful to the metallurgist in comparing the efficiencies of differently shaped laboratories, such as those with differently shaped hearths, differently shaped roof, differently arranged ports, etc. This conception of efficiency is that taken by Damour, and repeated by Queneau in his book on "Industrial Furnaces." We must be careful here not to compare the heat left in the laboratory with the heat of combustion alone. This would give

$$\frac{3,673,100}{6,202,300} = 0.59 = 59 \text{ per cent.}$$

But this is not the heat absorption of the laboratory alone, but is a function of the furnace as a whole, and depends largely on the efficiency of the regeneration accomplished by the regenerators. If we wish to obtain an idea of the perfection with which the laboratory of the furnace appropriates the heat passing into and through it, we must simply compare what it appropriates with what was sent into it. The percentage of this appropriation measures the efficiency of the laboratory for abstracting heat for the purpose of heating itself—a datum highly useful to know if the furnace is used simply for keeping a given working space up to a given temperature for an in-

definite time. If the heating of the furnace charge to the furnace heat is only a minor part of the useful work of the furnace, and keeping it at that temperature is the chief function of the furnace, then the relation of the heat thus appropriated and utilized to the total heat available to the laboratory, is a measure of the perfection of construction of the laboratory. This is the view of Damour and Queneau, and seems in some respects plausible.

However, if we are examining this question thus in detail, it appears to the writer that the view just explained and the conclusions derived thereform may really be the very opposite of the truth of the matter, and lead to entirely erroneous conclusions. If two exactly similar open-hearth furnaces are constructed, with the sole difference that the body of one is thicker walled than the body of the other, it is perfectly true that maintaining the same temperature in each will require more gas in the thin-walled furnace, but that it will abstract and radiate a considerably larger proportion of the heat passing through it than the thick-walled furnace. Yet, according to Damour and Queneau's principle, the thin-walled furnace would be considered as being the more efficient laboratory of the two. The truth is, we must either compute the heat left in the laboratories per unit of time per cubic meter of stock space in order to compare different furnaces, or else to get absolute efficiency compute the ratio of the heat passing into the laboratory with that absorbed usefully by the charge, viz.: in this case:

$$\frac{1,447,100}{13,968,100} = 0.104 = \mathbf{10.4} \text{ per cent.} \qquad (2)$$

(3) The temperature of the flame is that to which the products of combustion can be raised by the maximum heat which they contain. When perfectly consumed they contain the heat pre-existing as sensible heat in the hot gas and air, plus the heat of combustion. We have already calculated this total as 13,968,100 Calories. The mean heat capacity of the products of combustion, per 1° between 0° and t°, is:

CO^2	1,830 m^3 (0.37	+0.00022t)	= 677+0.4026t
O^2+N^2	14,628 m^3 (0.303	+0.000027t)	= 4,428+0.3950t
H^2O	1,500 m^3 (0.34	+0.00015t)	= 510+0.2250t
		Sum	= 5,615+1.0226t

Therefore,

$$t = \frac{13,968,100}{5,615+1.0226t}$$

Whence,

$$t = \mathbf{1,749}^\circ \qquad (3)$$

(4) If the excess air were not used, the 1,116 cubic meters of oxygen in the products, together with its corresponding quantity of nitrogen, 4,249 cubic meters, would be absent from the products of combustion, as would also some of the 211 cubic meters of water vapor. Since the oxygen in the air was 3,833 m^3 and the unused excess 1,116, the proportion of the 211 m^3 of water vapor belonging to the excess air was

$$211 \times \frac{1,116}{3,833} = 61 \text{ m}^3,$$

and the final products are CO^2 1,830 m^3, N^2 9,263 m^3 and H^2O 1,439 m^3.

The heat available will be the same as before from combustion, the same from preheated gas, but less from preheated air, because of the absence of the excess air. Since the air formerly used brought in 5,043,500, the proportion of this carried by the excess air is

$$5,043,500 \times \frac{1,116}{3,833} = 1,468,500,$$

leaving heat brought in by air in the second case the difference, viz.: 3,575,000, and the total heat in the products 13,968,100—1,468,500 = 12,499,600 Calories.

The mean heat capacity of the diminished quantity of products, per 1°, is, by the same methods as previously used, 3,973+0.8685t, and, therefore,

$$t = \frac{12,499,600}{3,973+0.8685t} = \mathbf{2,142}^\circ \qquad (4)$$

a gain of nearly 400° in maximum temperature, by cutting off the 40 per cent. excess of air which was being used.

Problem 74.

The new style Siemens furnace for small plants has the gas producers built in as part of the furnace, between the two regenerators. The furnace has only one regenerative chamber at each end for preheating the air used for burning the gas, while the latter comes to the ports hot directly from the producers. This plant is compact, economical of fuel, allows high temperatures to be reached, and occupies little floor space. As compared with the old style separate furnace and producer plant, it occupies about half the floor space, costs about 60 per cent. as much to build and uses about 60 per cent. as much coal. They are largely used abroad for melting steel for castings in small foundries and for melting pig iron for castings to be subsequently annealed to malleable castings.

Such a furnace melted a charge of 3,000 kilograms of cast iron in 4 hours, using 750 kilograms of coal. The cast iron was charged cold, at 0°, and run out melted at 1,450°, containing 300 Calories of sensible heat per kilogram. The coal and gases were of the following compositions:

Coal—C 75, H 5, O 12, H^2O 2; ash 6.
Producer Gas—CO 20, CO^2 5, CH^4 2, H^2 16, N^2 57.
Chimney Gas—CO^2 19, O^2 1.8, N^2 79.2.

The air coming to the furnace is at 0° and dry; a steam blower is used to run the producer, using 1 kilo. of steam per 6 kilos. of air blown in, and the raising of this steam requires 0.1 kilo of coal used under boilers. The ashes produced weigh 75 kilos. per heat run. Temperature of the hot producer gas entering the furnace laboratory 600°, of preheated air 1,000°, of products leaving laboratory 1,400°, of products entering chimney flue 350°.

Required:

(1) A heat balance sheet of the furnace as a whole.

(2) The net thermal efficiency of the furnace.

(3) The net thermal efficiency of the laboratory of the furnace.

(4) The net thermal efficiency of the regenerators.

(5) The theoretical flame temperature in the furnace.

Solution:

(1) Heat balance sheet per charge of 3,000 kilos.

Heat Available.

	Calories.
Calorific power of coal used in producers	5,248,500
" " " " " under boilers	398,900
	5,647,400

Heat Distribution.

In melted cast iron	900,000
In chimney products	768,950
Loss by unburnt carbon in ashes	243,000
Used for raising steam	398,900
Loss by radiation and conduction	3,336,550
	5,647,400

Calculation of the Heat Balance.

The heat of combustion of a kilogram of coal is not given, therefore must be calculated from its composition:

		Calories.
C $0.75 \times 8{,}100$	=	6,075
H $\left(0.05 - \frac{0.12}{8}\right) \times 34{,}500$	=	1,208
Calorific power to liquid water	=	7,283
Vaporization heat of water formed $(0.02 + 0.45) \times 606.5$	=	285
Calorific power to vapor of water	=	6,998
Of 750 kilos. in the producers	=	5,248,500

The coal used under the boilers can only be found by first finding how much steam was used, which in its turn can be gotten from the air blown in, and the nitrogen of this can be found from the total nitrogen in the producer gas. The volume of producer gas can be gotten from its carbon content per cubic meter and the known weight of carbon gasified. Or, turning this chain of reasoning the other way, if we subtract the carbon in the ashes from the carbon in the coal, the difference is the carbon entering the gases; this divided by the carbon in 1

cubic meter of chimney gas (calculated from its analysis) gives the volume of chimney gas, and by the carbon in 1 cubic meter of producer gas gives the volume of this gas used, from which the nitrogen in it can be calculated, which divided by 0.792 gives the volume of air used, from which its weight is obtained, thence the amount of steam used, and finally from this the amount of coal necessary to burn under boilers to raise this steam.

[In working most metallurgical problems the difficulty of finding the connection or succession of steps connecting the requirements with the data given is often easiest overcome by starting with the requirement in mind and noting from what other figure its value may be calculated, and thus passing backwards from one figure to another we finally arrive at one which can be found directly from the data given. The logical sequence of operations is thus disclosed and the problem is in reality solved; the following of the thread in the reverse direction, from data to requirement, involves calculations only, not hard thinking, and is usually a matter of the simplest arithmetic.]

The operations for calculating the steam used are as follows:

Carbon in coal in producers = 750×0.75	=	562.5 kg.
Carbon in ashes from producers = 75—45	=	30.0 "
Carbon in gases from producers	=	532.5 "
Carbon in producer gas per 1 m^3 = 0.27×0.54	=	0.1458 "
Producer gas per heat = $532.5 \div 0.1458$	=	3,652 m^3
Nitrogen in producer gas = $3{,}652 \times 0.57$	=	2,082 "
Air used in the producer = $2{,}082 \div 0.792$	=	2,629 "
	=	3,399 kg.
Carbon in chimney gas per 1 m^3 = 0.19×0.54	=	0.1026 "
Chimney gas per heat = $532.5 \div 0.1026$	=	5,190 m^3
Nitrogen in chimney gas = $5{,}190 \times 0.792$	=	4,110 "
Nitrogen from air used = 4,110—2,082	=	2,028 "
Air used to burn gas = $2{,}028 \div 0.792$	=	2,561 "
Weight of this air = $2{,}561 \times 1.293$	=	3,311 "
Weight of air used in producer	=	3,399 "
Weight of steam used in producer = $3{,}399 \div 6$	=	567 "
Weight of boiler coal used = 567×0.1	=	57 "
Calorific power of this coal = $6{,}998 \times 57$	=	398,900 Cal.

The heat in the melted cast iron is simply its weight times 300 = 300×3,000 = 900,000 Calories.

(2) The net thermal efficiency follows directly from this, as

$$\frac{900{,}000}{5{,}647{,}400.} = 0.16 = \mathbf{16} \text{ per cent.} \qquad (2)$$

(3) The gaseous products consist dry, as analyzed, of

CO^2	5,190×0.19 =	986 m^3
O^2	5,190×0.018 =	93 "
N^2	5,190×0.792 =	4,110 "

And in addition all the water formed from the coal, plus the steam used, a total of:

Water from coal = 0.47×750	= 352.5 kg.
Steam	= 566.5 "
Total water vapor in gases	= 919.0 "

Volume at standard conditions = 919÷0.81 = 1,135 m^3

At 350° these products carry out of the furnace heat as follows:

		Calories.
O^2+N^2	4,203×0.312 =	1,311
CO^2	986×0.447 =	441
H^2O	1,135×0.392 =	445
Average caloric capacity per 1°	=	2,197

Capacity per 350° = 768,950 Calories.

These same products would carry heat out of the laboratory of the furnace at 1,400° as follows:

		Calories.
O^2+N^2	4,203×0.341 =	1,433
CO^2	986×0.678 =	669
H^2O	1,135×0.550 =	624
Average caloric capacity per 1°	=	2,726

Capacity per 1,400° = 3,816,400 Calories.

The heat developed in the laboratory of the furnace by the combustion of the 3,652 m^3 of producer gas is

		Calories.
CO	0.20×3062	= 612
CH^4	$0.02 \times 8,598$	= 172
H^2	$0.16 \times 2,613$	= 418
Per 1 m^3		= 1,202

Per 3,652 m^3 = 4,389,700 Calories.

The 3,652 m^3 of gas comes into the laboratory of the furnace at 600°, and therefore carries in as sensible heat the following:

CO^2	$0.05 \times 0.502 = 0.0251$	Cal. per 1°
CH^4	$0.02 \times 0.512 = 0.0102$	" "
CO, N^2, H^2	$0.93 \times 0.319 = 0.2967$	" "
	$0.3320 \times 600 = 199.2$	Cal.

Per 3,652 m^3 = $199.2 \times 3,652$ = 727,480 Calories.

This does not count, however, the water vapor accompanying the producer gas. This is best determined from the fact that the total hydrogen in the coal and steam used in the producer must appear as hydrogen in the producer gas in some form or other, and whatever is not present in the dry producer gas must be in the water vapor accompanying it. The amount of this and the heat it carries into the laboratory of the furnace are thus determined:

Hydrogen in 750 kg. coal = 750×0.0522	=	39.15 kg.
Hydrogen in steam used = $567 \div 9$	=	63.90 "
Hydrogen going into producer gases	=	102.15 "
Hydrogen in dry producer gases, $3,652 \times 0.20 \times 0.09$	=	65.74 "
Hydrogen in producer gas as vapor of water	=	36.41 "
Water vapor in producer gas	=	327.7 "
Volume of this vapor	=	405 "
Heat in this at 600°, $405 \times 0.43 \times 600$	=	104,500 Cal.
Total heat in moist producer gas, $727,480 + 104,500$	=	831,980 "

We must also calculate the heat brought into the laboratory of the furnace by the preheated air, at 1,000°, used for combustion. This is

$2,561\ m^3 \times 0.330 \times 1,000$ = 845,130 Calories.

It follows from the above calculations that the laboratory of the furnace receives per heat of steel:

		Calories.
From hot producer gas at 600°	=	831,980
From preheated air at 1,000°	=	845,130
From combustion	=	4,389,700
Total	=	6,066,810

Of this total there is rejected in the hot products at 1,400°, 3,816,400 Calories, leaving in the laboratory of the furnace 2,250,410 Calories.

According to the view of Damour and Queneau (Industrial Furnaces, page 56) the ratio of the heat thus left in the body of the furnace to the calorific power of the fuel used, measures the thermal efficiency of the furnace. According to that view this new style Siemen's furnace has an efficiency of

$$\frac{2,250,410}{5,647,400} = 0.400 = 40.0 \text{ per cent.}$$

This figure, however, is an illusive one. It enables us to compare two furnaces and see which regenerates the waste heat best, or which furnace laboratory is designed best so as to catch and retain most of the heat furnished to it; but the real question is the comparison of different laboratories as to their net melting efficiency. This laboratory abstracts from the heat supply furnished to it 2,250,410 Calories, and furnishes to the steel 900,000 Calories. Its proportion of usefully applied heat to heat appropriated is, therefore:

$$\frac{900,000}{2,250,410} = 0.400 = \mathbf{40.0} \text{ per cent.} \qquad (3)$$

The laboratory of the furnace therefore loses by radiation 60 per cent. of the heat which it abstracts from the gases, or 2,250,410 − 900,000 = 1,350,410 Calories. This is 24 per cent. of the calorific power of the coal used.

(4) The regenerators receive 3,816,400 Calories from the laboratory of the furnace, and return to it the heat in the preheated air at 1,000°, viz.: 845,130 Calories. If we call the ratio of these two the efficiency of the regenerators we have

$$\frac{845,130}{3,816,400} = 0.222 = 22.2 \text{ per cent.}$$

If, however, we charge them only with the heat actually left in them by the hot products, entering 1,400° and leaving at 350°, we have an efficiency of

$$\frac{845{,}130}{3{,}816{,}400—768{,}950} = 0.277 = 27.7 \text{ per cent.} \qquad (4)$$

As long as the chimney gases are near in temperature to 300°, we can use the latter form of calculation as representing the real efficiency of the regenerator. The regenerators, therefore, lose by radiation and conduction to the air 2,202,320 Calories, which is 72.3 per cent. of the heat left in them by the hot gases and 39 per cent. of the calorific power of the coal used.

(5) The flame temperature is that to which the 6,066,810 Calories available in the laboratory of the furnace will raise the products of combustion. The average mean specific heat of the latter per 1° is:

$$\begin{array}{lrl} CO^2 & 986\ m^3 \times (0.37 + 0.00022t) & = 365 + 0.2169t \\ O^2 + N^2 & 4{,}203\ m^3 \times (0.303 + 0.000027t) & = 1{,}274 + 0.1135t \\ H^2O & 1{,}135\ m^3 \times (0.34 + 0.00015t) & = 386 + 0.703t \\ & & \text{Sum} = 2{,}025 + 0.5008t \end{array}$$

$$\text{Therefore} \qquad t = \frac{6{,}066{,}810}{2{,}025 + 0.5008t}$$

$$\text{Whence} \qquad t = 2{,}003 \qquad (5)$$

Problem 75.

In an basic lined open-hearth furnace using the Monell process, 50 short tons of melted pig iron, at 1,300°, is run upon 30,000 pounds of Lake Superior iron ore (90 per cent. Fe^2O^3, 10 per cent. SiO^2) lying on the hearth and previously heated to 1,300°. There is 2,000 pounds of burnt lime lying on the ore to help to form slag. The ore reacted quickly, almost violently, on the melted pig iron, so that at the close of the reaction, in 20 minutes, the slag could be run off. The pig iron contained,

	On Running in.	*After the Reaction*
Carbon	3.50	3.00
Silicon	2.00	0.00
Phosphorus	0.75	0.00
Manganese	0.50	0.00
Iron	93.25	97.00

The oxidation of C, Si, P and Mn may be assumed as being produced first by reducing all Fe^2O^3 present to FeO, and completed by the reduction of *some* FeO to Fe. The carbon is assumed oxidized in the reaction to CO, although this CO may be subsequently partly burned to CO^2 by excess air in the furnace.

Required:

(1) The amount of iron reduced into the bath.

(2) The weight and percentage composition of the slag formed.

(3) The items of heat evolved and absorbed in the reaction.

Solution:

(1) We cannot make a simple, direct solution, because the weight of the metal after the reaction, analysis of which is given, is not known. The inexperienced calculator might be tempted to say that there was 3.50—3.00 = 0.50 per cent. of carbon oxidized, 2.00 per cent. of silicon, 0.75 per cent. of phosphorus and 0.50 per cent. of manganese, calculate the weights of these, reckon up the oxygen they would absorb in being oxidized, and thus get at the amount of Fe^2O^3 reduced to FeO and FeO reduced to Fe. This would be correct as far as silicon, manganese and phosphorus are concerned, because they are entirely oxidized, but incorrect for the weight of carbon, because the 3.00 per cent. not oxidized is per cent. of the final bath, which is of different weight from the original one, and, therefore, we are in error in subtracting 3.00 from 3.50. Being confronted with this dilemma we can see, however, that if we only knew the weight of the bath after the reaction we could calculate correctly how much carbon is in it, thence get the correct weight of carbon oxidized, then the correct amount of oxygen absorbed in the reaction, and from this the weight of iron reduced into the bath. We could also get the latter quantity more simply by finding the iron present in the bath

after the reaction (97 per cent.), and subtracting from it the iron in the original bath. We thus have two ways of getting the same requirement if we only know the weight of the bath. In such a case the mathematical key to the situation is, of course, to let X represent the weight of the bath, and work out the amount of iron reduced into the bath by the two methods, getting the result expressed in each case in terms of X. Since the two expressions represent the same quantity, we put them equal to each other and solve for X. Having obtained X, we substitute it in either expression and get the result asked for.

Let X be the weight of the bath after the reaction, in pounds; the bath before the reaction weighs 100,000 pounds.

Oxidized out:

Carbon (100,000×0.035)—X 0.03	= 3,500—0.03 X	pounds.
Silicon 100,000×0.02	= 2,000	"
Phosphorus 100,000×0.0075	= 750	"
Manganese 100,000×0.005	= 500	"
Oxygen required:		
For carbon (3,500—0.03 X) 16/12	= 4,677—0.04 X	pounds.
For silicon 2,000×32/28	= 2,286	"
For phosphorus 750×80/62	= 968	"
For manganese 500×16/55	= 145	"
	Sum = 8,076—0.04 X	pounds.

Oxygen supplied:

If all Fe^2O^3 of ore (27,000 pounds) were reduced to FeO = 27,000×16/160 = 2,700 pounds.

If all Fe^2O^3 of ore were reduced to Fe 27,000×48/160 = 8,100 pounds.

We thus see that we will certainly require more oxygen than the Fe^2O^3 can give up in becoming all FeO, but not as much as would be given up if it all became Fe. If all the Fe^2O^3 were considered first reduced by the reaction to FeO, giving up 2,700 pounds of oxygen, the reaction will still require the furnishing of

$$(8{,}076—0.04\ X)—2{,}700 = 5{,}376—0{,}04\ X \text{ pounds.}$$

of oxygen, which would have to be furnished by FeO becoming

Fe. In that reduction, however, 72 parts of FeO gives up 16 of oxygen in becoming 56 Fe. The reduced Fe will be, therefore, 56/16 of the weight of oxygen thus furnished, and therefore,

$$\text{Reduced Fe} = 56/16\ (5{,}376 - 0.04\ X) \text{ pounds.}$$
$$= 18{,}816 - 0.14\ X \text{ pounds.}$$

The same quantity is obtained more directly as follows:

Fe in original bath $100{,}000 \times 0.9325$	=	93,250 pounds.
Fe in bath after reaction	=	$0.97\ X$ pounds.
Therefore, Fe reduced	=	$0.97\ X - 93{,}250$ lbs.

These two expressions represent the same thing, and, therefore,

$$18{,}816 - 0.14\ X = 0.97\ X - 93{,}250$$

Whence $X = 100{,}960$

And the reduced iron $= 0.97\ X - 93{,}250 = 4{,}681$ pounds. (1)

(2) The ore used contains altogether

Fe $= 27{,}000 \times 112/160$	=	18,900 lbs.		
Fe reduced to metallic state	=	4,681 "		
Fe remaining in slag as FeO	=	14,219 "		
Weight of FeO $= 14{,}219 \times 72/56$	=	18,282 "	=	61.1 per cent.
Weight of $P^2O^5 = 750 + 968$	=	1,718 "	=	5.7 "
Weight of MnO $= 500 + 145$	=	645 "	=	2.1 "
Weight of CaO	=	2,000 "	=	6.7 "
Weight of $SiO^2 = 3{,}000 + 4{,}286$	=	7,286 "	=	24.4 "
Total weight of slag	=	29,931 "		(2)

(3) The physical data available do not permit of calculating the actual heat of the reaction at 1,300°, since many of the specific heats needed are lacking. We will therefore foot up the items of heat evolution and absorption uncorrected for temperature, which is the only thing to be done under the circumstances.

	Heat Evolution.	*Calories*
Si to SiO^2	$2{,}000 \times 7{,}000$	= 14,000,000
P to P^2O^5	$750 \times 5{,}892$	= 4,419,000
Mn to MnO	$500 \times 1{,}653$	= 826,500
C to CO	$471 \times 2{,}430$	= 1,144,500
SiO^2 to FeO. SiO^2	$7{,}286 \times 144$	= 1,049,200
CaO to 3CaO. P^2O^5	$2{,}000 \times 949$	= 1,898,000
	Total =	23,337,200

Heat Absorption.

		Calories.
Fe^2O^3 to FeO	18,900 × 573	= 10,829,700
FeO to Fe	4,681 × 1,173	= 5,490,800
Fe^3C to Fe^3+C	471 × 705 (?)	= 332,000 (?)
FeSi to Fe+Si	2,000 × 931 (??)	= 1,682,000 (??)
Fe^3P to Fe^3+P	750 × 1,400 (??)	= 1,050,000 (??)
		Sum = 19,564,500

These calculations, therefore, show a minimum surplus of heat in the reaction of 23,337,200 − 19,564,500 = 3,772,700 Cal., an amount which would raise the temperature of the slag and resulting metal approximately 100° C. above the 1,300° at which the reacting materials came together. The quantity above marked (?) is a little doubtful in amount, but those marked (??) are very doubtful, perhaps may not exist at all. If these are omitted from the heat absorption the surplus heat is increased some 50 per cent. of its value, and the rise in temperature might be in the neighborhood of 150°. Further, some of the CO formed by the oxidation of carbon may be burned to CO^2 close to the surface of the bath, by free oxygen in the furnace, still further increasing the rise in temperature.

The conclusion from these calculations and discussions is that the pig iron and ore reaction in the Monell process is a heat evolving reaction, which, independently of the heating effect of the fuel used by the furnace, could increase the temperature of the contents of the furnace at least 100°, and possibly 150°. It would be highly interesting to have a typical heat such as this followed closely with a good reliable pyrometer, so as to check the indications of the thermochemical study of the process.

CHAPTER XII.

THE ELECTROMETALLURGY OF IRON AND STEEL.

Electrical methods may enter into the extraction of a metal from its ores either as electrolytic or as electrothermal processes. Electrolytic processes are those in which the electric current is used for its electrolytic action, *i.e.*, for its electrical decomposing and depositing properties; electrothermal processes are such as use the current merely as a source of heat, to furnish the sensible heat and high temperature necessary for melting materials or for bringing about chemical reactions. So far electrolytic processes have entered the metallurgy of iron only as used by Burgess for electrolytically refining nearly pure iron in an aqueous electrolyte and depositing chemically pure iron; the electrolysis of fused iron salts has not been practically utilized. Up to the present, electrothermal processes are in commercial use for melting together wrought iron and cast iron to make steel, also for keeping cast iron melted while its impurities are being extracted by oxidation; the electrothermal reduction of iron ores to cast iron has been proved technically possible, and may in some places prove commercially practicable.

Electrothermal Reduction of Iron Ores.

If the electric current is used to furnish the heat energy necessary to reduce iron ore, it cannot displace the reducing agent—carbon. In ordinary blast furnace practice the carbon is first burned to provide the heat necessary to smelt down the pig iron and slag, and the product of this incomplete combustion—CO—abstracts oxygen from the ore. The two equations are practically:

At the tuyeres—

$$30C + 15O^2 + 57.15\ N^2 = 30CO + 57.15\ N^2$$

Reduction:

$$4Fe^2O^3 + 30CO + 57.15\ N^2 = 12CO^2 + 18CO + 57.15\ N^2 + 8Fe$$

These equations show us that to produce 8Fe = 448 parts, 30C = 360 parts of carbon is the minimum necessary, which is first burned to CO at the tuyures, and then the producer gas thus formed (N^2 and CO) reduces the iron oxides above. If the heat for fusion is furnished electrically, the first combustion is unnecessary, all blowing in of air is dispensed with and the reaction taking place is:

$$14Fe^2O^3 + 30C = 12CO^2 + 18CO + 28Fe$$

And we have 28Fe = 1,568 parts reduced by 30C = 360 parts, a consumption of less than one-third as much carbon as is required in the blast furnace. The operation consists, therefore, in mixing iron ore and carbon so that for every part of iron present about 0.25 parts of carbon is present, using the proper quantity of limestone or other material to flux the gangue of the ore to a fusible slag, and then furnishing electrically the heat necessary to cause the chemical reaction, melt down the resulting iron and slag, and supply radiation losses. The gases resulting from this electrical reduction are combustible, just as the gases from the blast furnace, and since there is no blast to be heated they can very well be utilized to preheat the charges coming into the furnace, and thus save some of the electrical energy needed.

Problem 76.

A magnetite ore contains:

	Per Cent.		*Per Cent.*
Fe^2O^3	60.74	MgO	5.50
FeO	17.18	P^2O^5	0.04
SiO^2	6.60	S	0.57
Al^2O^3	1.48	CO^2	2.05
CaO	2.84	H^2O	3.00

It is to be mixed with pure carbon (charcoal fines) and a suitable flux; the fixed carbon being 0.25 per cent. of the iron present; the flux silica sand, so as to make a slag with 33 per cent. of SiO^2. Neglect the ash and assume 10 per cent. of moisture in the charcoal. Assume also:

(*a*) The pig iron to contain 4 per cent. C, 3.5 per cent. Si, 92.4 per cent. Fe.

(*b*) The slag and pig iron to contain at tapping 600 and 400 Calories of heat respectively.

(*c*) The heat losses by radiation, etc., to be 30 per cent. of the total heat requirement of the furnace.

(*d*) The hot gases to escape at 300° C.

(*e*) The iron to be completely reduced into the pig iron.

(*f*) The sulphur to go entirely into the slag as CaS.

Requirements:

(1) The weights of ore, flux and charcoal dust needed per 1,000 kg. of pig iron produced.

(2) A balance sheet of materials entering and leaving the furnace.

(3) A heat balance sheet of the furnace.

(4) The number of kilowatt days of electrical energy required per metric ton of pig iron produced.

Solution:

(1) The ore must supply 924 kg. of iron. But 100 parts of ore contains iron as follows:

		Kg.
In Fe^2O^3	$60.74 \times 112/160$	= 42.52
In FeO	$17.18 \times 56/72$	= 13.36
	Sum =	55.88 (1)

Ore required per 1,000 kg. of pig iron:

$$924 \div 0.5588 = \mathbf{1{,}654} \text{ kg.}$$

The slag-forming ingredients from this amount of ore are as follows:

	Kg.
Al^2O^3 $1{,}654 \times 0.0148$	= 24.6
MgO $1{,}654 \times 0.0550$	= 91.0
CaO $1{,}654 \times (0.0284 - 0.0057 \times 56/32)$ $= 1{,}654 \times 0.0184$	= 30.4
SiO^2 $(1{,}654 \times 0.0660) - (35 \times 60/28) = 109.2 - 75$	= 34.2
CaS $1{,}654 \times (0.0057 \times 72/32)$	= 21.2
Sum =	201.4

If x parts of SiO^2 sand are added to these, the total weight

of slag will be $201.4+x$, of SiO^2 in it $34.2+x$. And since the SiO^2 is to be 33 per cent. of the weight of slag, then

$$34.2+x = 0.33\ (201.4+x)$$

Whence $x = 48$ kg. (1)

The charcoal dust used must contain fixed carbon equal to 0.25 of the iron present, *i. e.*,

$$924 \times 0.25 = 231 \text{ kg.}$$

And since it is 90 per cent. fixed carbon the dust required is:

$$231 \div 0.90 = \mathbf{257} \text{ kg.}$$

Charges.	*Pig Iron.*	*Slag.*	*Gases.*
Ore.....**1654** Kg.			
Fe^2O^3.....1004.6	Fe.....703.2	.....	O.....301.4
FeO.....284.2	Fe.....221.0	.....	O.....63.2
SiO^2.....109.2	Si.....35.0	SiO_2.....34.2	O.....40.0
Al^2O^3.....24.6	.....	Al_2O_3.....24.6	.....
CaO.....46.9	.....	CaO.....30.4	O.....4.7
MgO.....91.0	.....	MgO.....91.0	.....
P^2O^5.....0.6	P.....0.3	Ca.....11.8	O.....0.3
S.....9.4	.....	S.....9.4	.....
CO_2.....33.9	.....	.....	CO_2.....33.9
H^2O.....49.6	.....	.....	H_2O.....49.6
Flux.....**48** Kg.			
SiO^2.....48.0	.....	SiO_2.....48.0	.....
Charcoal....**257** Kg.			
C.....231.0	C.....40.0	.....	C.....191.0
H^2O.....26.0	.....	.....	H_2O.....26.0
1959.0	999.5	249.4	118.1

(3) Heat available is the heat of oxidation of carbon plus that furnished by the electric current. The charge gives up to the carbon, as shown on the balance sheet, $301.4+63.2+40.0+4.7+0.3 = 409.6$ kg. of oxygen. The 191 kg. of carbon burned would take $191 \times 16/12 = 254.7$ kg. of oxygen to burn it to CO, leaving 154.9 kg. of oxygen to burn CO to CO^2. This would burn $154.9 \times 28/16 = 271.1$ kg. of CO to CO^2.

The heat of formation of the slag may be taken as approxi-

mately 150 Calories per kg. of contained $SiO^2+Al^2O^3$. The heat of combination of carbon with the iron is a doubtful quantity, which may be taken at 705 Calories per kilogram of carbon. The formation of CaS gives 2,947 Calories per kilogram of sulphur.

Letting the heat furnished by the electric current = x, and neglecting the heat of oxidation of the small amount of electrode carbon consumed, we have:

Heat Available.

		Calories.
Supplied by electric current:		x
Oxidation of C to CO	$191\times2,430$ =	434,130
Oxidation of CO to CO^2	$271.1\times2,430$ =	658,770
Formation of silicate slag	106.8×150 =	16,020
Formation of CaS	$9.4\times2,947$ =	27,700
Formation of Fe^3C	$40.\times 705$ =	28,200
	Sum =	$1,194,820+x$

Heat Distribution.

	Calories.
Reduction of Fe from Fe^2O^3	
$703.2\times1,746$	= 1,229,790
Reduction of Fe from FeO	
$221.0\times1,173$	= 259,230
Reduction of Si from SiO^2	
$35.0\times7,000$	= 245,000
Reduction of P from P^2O^5	
$0.3\times5,892$	= 1,770
Reduction of Ca from CaO	
$11.8\times3,288$	= 38,800
Expulsion of CO^2 from ore	
$33.9\times1,026$	= 34,780
Evaporation of H^2O from charges	
75.6×606.5	= 45,850
Sensible heat in gases, at 300°	
CO 174.6 kg. = 138 m^3	
$\times0.311$ = 42.9	

CO^2 459.9 kg. = 232 m^3
× 0.436 = 101.1
H^2O 75.6 kg. = 93 m^3
× 0.385 = 35.8

$179.8 \times 300 = 53{,}940$
Sensible heat in slag $249.4 \times 600 = 149{,}640$
Sensible heat in pig iron $1{,}000 \times 400 = 400{,}000$
Loss by radiation, etc., $0.30\ (1{,}194{,}820 + x) = 358{,}450 + 0.3x$

Sum total = $2{,}817{,}250 + 0.3x$

Equating the heat available and accounted for we have:

$$1{,}194{,}820 + x = 2{,}817{,}250 + 0.3\ x.$$

Whence $x = 2{,}317{,}760$ Calories.

And the sum total of heat requirement is

3,512,580 Calories,

of which the electric current supplies

$$\frac{2{,}317{,}760}{3{,}512{,}580} = 0.66 = \mathbf{66} \text{ per cent.} \qquad (3)$$

(4) A kilowatt-day of electricity is equal to

$$0.239 \times 60 \times 60 \times 24 = 20{,}650 \text{ Calories.}$$

There is, therefore, required per ton of pig iron produced:

$$\frac{2{,}317{,}760}{20{,}650} = \mathbf{112} \text{ kilowatt days.} \qquad (4)$$

This figure might be materially reduced by using the waste gases to warm up the charges entering the furnace. It is also possible that in a properly designed shaft the gases passing out might contain nearly equal volumes of CO and CO^2, instead of 3CO to 2CO, as assumed in this problem, from best ordinary blast furnace practice. Any greater utilization of the heat-producing power of the carbon would decrease the electrical energy required; the above calculated value is given as a safe figure for this ore on which to base working calculations.

Problem 77.

At Sault Sainte Marie, Canada, roasted pyrrhotite ore was smelted with the addition of limestone and charcoal fines. The mixture used contained 400 pounds of ore, 110 pounds charcoal dust and 85 pounds limestone. The analyses of each of these materials was:

Roasted Ore.		*Limestone.*		*Charcoal Dust.*	
Fe^2O^3	65.43	CaO	52.00	Fixed C	55.90
CuO	0.51	MgO	2.10	Vol. matter	28.08
NiO	2.84	Fe^2O^3	0.60	Moisture	13.48
SiO^2	10.96	Al^2O^3	0.21	Ash	2.54
Al^2O^3	3.31	SiO^2	1.71		
CaO	3.92	P^2O^5	0.01		
MgO	3.53	SO^3	0.13		
SO^3	3.90	CO^2	43.15		
P^2O^5	0.03				
H^2O	5.57				

Using 165.65 kilowatts effective electric energy for 56 hours 20 minutes, there was produced 7,336 pounds of nickeliferous pig iron and 5,062 pounds of slag, having the following average compositions:

Pig Iron.		*Slag.*	
C	3.05	SiO^2	16.44
Si	5.24	Al^2O^3	13.86
S	0.01	CaO	42.87
P	0.05	MgO	8.80
Cu	0.81	CaS	13.34
Ni	3.94	FeO	0.84
Fe	86.90	Undetermined	3.85

Requirements:

(1) A balance sheet of materials entering and leaving the furnace.

(2) A heat balance sheet of the furnace, making necessary assumptions where data is not furnished.

(3) The thermal efficiency of the furnace.

Solution:

(1) The amount of ore used may be calculated either from the iron, the nickel or the copper. The nickel and copper are the easiest to use, because there is supposed to be none of

them in the slag, but they are the least reliable, because present in such small amount. The pig-metal contains $7,336 \times 0.81 = 59.4$ pounds of copper, and since the roasted ore contains $0.51 \times \frac{63.6}{79.6} = 0.41$ per cent. copper, the weight of ore used, on this basis, would be $59.4 \div 0.0041 = 14,493$ pounds. As for nickel, the pig-metal contains $7,336 \times 0.0394 = 289$ pounds of nickel, and since the roasted ore contained $2.84 \times \frac{59}{75} = 2.23$ per cent., the weight of this used should have been $289 \div 0.0223 = 12,960$ pounds. These figures differ so much that we will make the calculation on the basis of the iron. There is iron present as follows:

	Pounds.
In the pig iron $7,336 \times 0.8690$	= 6,375
In the slag $5.062 \times 0.0084 \times 56/72$	= 33
Total in products	= 6,408
In 100 pounds of ore 65.43×0.7	= 45.80
In 21 pounds limestone $21. \times 0.0060 \times 0.7$	= .08
In 27.5 pounds of charcoal $27.50 \times 0.0025 \times 0.7$	= .04
In charge, per 100 pounds of ore used	= 45.92

Therefore, ore necessary to supply the iron in products:

	Pounds.
$6,408 \div 0.459$	= 13,961

with which will be used:

Charcoal = $13,961 \times 110/400$	= 3,839
Limestone = $13,961 \times 85/400$	= 2,967

We are now ready to construct the balance sheet as soon as we assume probable values for the composition of the volatile matter and ash of the charcoal. The ash might be taken as containing on an average: K^2O 15 per cent., CaO 40, MgO 20, MnO 15, and Fe^2O^3 10 per cent. The volatile matter is due to insufficient charring, and the gases given off on heating may be assumed as, by volume, CO^2 25 per cent., CO 15, H^2

50, CH^4 10. This would make the volatile matter to contain, in per cents. by weight, carbon 33.7, oxygen 58.5, hydrogen 7.8 per cent. (The verification of this last statement is a nice little exercise in chemical arithmetic.) The full statement of the elementary composition of the charcoal, for use in making the balance sheet, is therefore:

	Per Cent.	
Fixed carbon	55.90	
Volatile carbon	9.46	28.08%
Volatile hydrogen	2.19	
Volatile oxygen	16.43	
Moisture	13.48	
K^2O	0.38	2.54%
CaO	1.02	
MgO	0.51	
MnO	0.38	
Fe^2O^3	0.25	

Balance Sheet, per 7,336 Lbs. Pig-metal.

Charges.		*Pig-metal.*		*Slag.*		*Gases.*	
Roasted Ore.	**13,961**						
Fe^2O^3	9,135	Fe	6,375	FeO	25	O	2,375
NiO	397	Ni	289	NiO	28	O	80
CuO	71	Cu	59			O	12
SiO^2	1,530	Si	384	SiO^2	1,091	O	55
Al^2O^3	461			Al^2O^3	461		
CaO	547			CaO	166	O	109
MgO	493			MgO	493		
SO^3	545	S	1	CaS	490	O	327
P^2O^5	4	P	4			O	0
H^2O	778					H^2O	778
Limestone	**2,967**						
CaO	1,543			CaO	1,542	O	0
MgO	62			MgO	62		
Fe^2O^3	18			FeO	16	O	2
Al^2O^3	6			Al^2O^3	6		
SiO^2	51			SiO^2	51		
P^2O^5	0			P^2O^5	0		
SO^3	4			CaS	4		
CO^2	1,280					CO	1280
Charcoal dust	**3,839**						

Fixed C.....	2,146	C.....224	.....	C.....1,922
Vol. C.....	363	.....	.....	C.....363
Vol. H.....	84	.....	.....	H..... ..84
Vol. O.....	631	.....	.....	O.....631
H^2O.....	518	.....	.....	H_2O.....518
K^2O.....	15	.....	K^2O.....15	.....
CaO.....	39	.....	CaO.....39	.....
MgO.....	20	.....	MgO.....20	.....
MnO.....	15	.....	MnO.....15	.....
Fe^2O^3.....	10	.....	FeO..... 9	O..... 1
Electrode....	66			
C.....	66	.....	.....	C.....66
	20,828	7,336	4,533	8,962

There is a lack of close correspondence between the weights and compositions of slag, as observed and as calculated, due evidently to inaccurate sampling and analyses of the roasted ore and slag.

(2) From the balance sheet we can deduce the heat evolved and absorbed in the chemical reactions in the furnace. The more involved items are calculated as follows:

Oxidation of carbon to CO: All the carbon put into the furnace as fixed carbon goes out as either CO or CO^2, except that going into the pig iron. The carbon burnt to CO in the furnace may be, therefore, taken as $1,922+66 = 1,988$ pounds, evolving $1,988\times2,430 = 4,830,800$ pound-Calories.

Oxidation of CO to CO^2: There is given up in the furnace, by the reductions accomplished, 3,021 pounds of oxygen, of which $1,988\times16/12 = 2,651$ pounds would burn fixed carbon to CO, as above shown, leaving 370 pounds to burn CO to CO^2. This would oxidize $370\times28/16 = 648$ pounds of CO to CO^2, which would evolve $648\times2,430 = 1,574,300$ pound-Calories.

Heat energy of electric current: One kilowatt-second is 0.239 kilogram Calories, or 0.527 pound-Calories. The current being on 56 hours, 20 minutes, or 202,800 seconds, the heat equivalent of the current used is:

$0.527\times202,800\times165.65 = 17,704,000$ pound-Calories.

Heat in escaping gases: We are here confronted with the fact that no observation of the temperature of these was given.

There is no essential reason why they should escape very hot from the furnace, if properly run and conducted, so we will assume a maximum temperature of 500° C. The gases would consist of 0,958+2,651 − 648 = 4,061 pounds of CO and 648+ 370 = 1,018 pounds of CO^2, from the oxidation of fixed carbon in the furnace; plus 1,280 of CO^2 from the limestone, and 666 pounds CO^2, 254 pounds CO, 97 pounds CH^4 and 60 pounds of H^2 from the volatile matter of the charcoal. To these must be added 1,290 pounds of water vapor. The heat is therefore

CO	4,315 lbs. = 54,800 ft³ × 0.304 =	16,650	oz. Cal.
CO^2	2,964 lbs. = 23,950 ft³ × 0.480 =	11,500	"
CH^4	97 lbs. = 2,150 ft³ × 0.490 =	1,050	"
H^2	60 lbs. = 10,700 ft³ × 0.304 =	3,250	"
H^2O	1,290 lbs. = 25,500 ft³ × 0.415 =	10,550	"
	Sum = 117,100 ft³	43,000	" per 1°
		= 21,500,000	" per 500
		= 1,343,750	lb.-Cal.

The other items of the heat balance sheet are almost self-explanatory, and the complete balance is as follows:

Heat Available.

	Pound-Cal.
Energy of the electric current	= 17,704,000
Oxidation of C to CO	= 4,830,800
Oxidation of CO to CO^2	= 1,574,600
Combination of C with Fe^3 224×705	= 157,900
Combination of Ca with S 220×2,947	= .648,300
Formation of silico-aluminate slag ($SiO^2 + Al^2O^3$) 1 609×150	= 241,400
Total	= 25,157,000

Heat Distribution.

Reductions:		
Fe^2O^3 to Fe	6,375×1,746 =	11,130,750
NiO to Ni	289×1,051 =	303,750
CuO to Cu	59× 593 =	35,000
SiO^2 to Si	384×7,000 =	2,688,000
SO^3 to S	218×2,872 =	626,100
P^2O^5 to P	4×5,892 =	23,550
CaO to Ca	274×3,288 =	900,900
Fe^2O^3 to FeO	50× 446 =	22,300

Expulsion of CO^2 from flux:		
	$1,280 \times 1,026$ =	1,313,300
Evaporation of H^2O	$1,290 \times 606.5$ =	783,400
Sensible heat in gases	=	1,343,750
Sensible heat in pig iron	$7,336 \times 400$ =	2,934,400
Heat in slag	$4,533 \times 600$ =	2,719,800
Loss by radiation, conduction, etc.	=	332,000
	Total =	25,157,000 (2)

(3) The essential work done by the furnace is the reductions, evaporation of moisture and decomposition of carbonates. The heat in slag, iron, gases and radiation loss are all susceptible of diminution or of being more or less returnable to the furnace. The usefully applied heat is, therefore, 17,827,050 pound-Calories. To produce this there was consumed the 25,157,000 pound-Calories actually generated, and there was wasted 13,390,000 pound-Calories, the calorific power of the gases escaping from the furnace, which should have been generated or might be utilized, making a total of 38,527,000 pound-Calories disposable.

The working thermal efficiency over all was therefore:

$$\frac{17,827,050}{38,527,000} = 0.46 = \mathbf{46} \text{ per cent.} \qquad (3)$$

Production of Steel.

There are three methods of producing steel electrically which are practicable. First, the electric furnace may replace the crucible simply as a melting apparatus, in producing a cast steel from cemented bars; second, the electric furnace may replace the crucible or open-hearth furnace as an apparatus in which to melt together wrought iron and pure cast iron, such as washed pig metal, although in this operation, the electric furnace is more like the crucible method, in that there is not necessarily any oxidation of the metal or of its impurities in the operation; third, the electric furnace may be used to melt or keep melted cast iron, while its impurities are oxidized out by additions of iron ore, in this operation resembling the Uchatius method of making crucible steel or the "pig and ore" process of making steel in the open-hearth furnace.

The particular advantages possessed by the electric furnace processes are, compared with the crucible process, the larger quantities in which the steel can be made in one operation, the absence of carbon in the furnace lining, thus controlling better the carbon and silicon in the steel, and the higher temperature enabling a more basic slag to be kept fluid and the sulphur to be better eliminated; the advantages compared with the open-hearth furnace are the absence of gases of combustion in contact with the metal, and the higher temperature available, which permits of very basic, refractory slags being made and kept thinly fluid, and thus gives better control of sulphur and phosphorus. In addition to these, in both cases, may be mentioned the commercial advantages, for the saving in crucibles alone makes the electric furnace superior in this respect to the crucible process, and the electric furnace can compete successfully as regards cost with the regenerative open-hearth furnace wherever water power costs less than $10.00 per horse-power-year and coal costs over $5.00 per ton.

A particular point to be noted is, that when heating by combustion is used the efficiency of the absorption of heat by the charges decreases very rapidly as the temperature gets higher. For instance, if a cold ingot of iron is placed in a furnace the temperature of which is 1,500°, the iron absorbs heat with very great rapidity from the start up to, say, 1,000°; but with decreasing rapidity thereafter. The rate of transfer of heat from the gases to the iron is proportional to the difference of temperature, and is some fifteen times as fast when the iron is at 0° as when it is at 1,400°. If the efficiency of the heating by furnace gases is, say, 25 per cent. in bringing metal up to 1,500°, it is likely that the distribution of this efficiency is proportioned about as follows:

Heating from 0° to 500°.....45 per cent. efficiency.
Heating from 500° to 1,000°.....27 per cent. efficiency.
Heating from 1,000° to 1,500°..... 3 per cent. efficiency.

On the other hand, the conversion of electrical energy into heat in the substance of the material to be heated is not a contact or transfer phenomenon, but a thermodynamically frictionless transfer of 100 per cent. efficiency, and equally so at the highest as at the lowest temperatures. Only radiation and

conduction losses need be considered, the problem is not how much heat can you *get* into a body but how much can you *keep* in; it is already all in, 100 per cent. of it, to start with. In a large, properly designed electric furnace the radiation and conduction losses of heat, even working to the highest temperatures, can be kept at 15 to 25 per cent. of the total heat generated, giving an efficiency of 75 to 85 per cent.

It may very well be, that there are places where the relative prices of coal and electric power are such that coal is the cheaper for heating to 500°, at 45 per cent, efficiency, or to 1,000° at 36 per cent. efficiency, or even to 1,500°, at 25 per cent. efficiency, but that the combination of heating by fuel to 1,000° at 36 per cent. efficiency and then by electricity from 1,000° to 1,500°, at 70 per cent. efficiency, would be the cheaper plan, or even by fuel to 500°, at 45 per cent. efficiency, and then by electricity from 500° to 1,500°, at, say, 75 per cent. efficiency, would be commercially advantageous.

Illustration: Steel bars are to be melted in an electrical furnace. It takes 300 Calories effective in the steel per kilogram to heat it to a tapping heat; the electric furnace supplies this at a net thermal efficiency of 75 per cent. To heat the bars to 750°, cherry red, without melting them, requires, 88 Calories, or 29 per cent. of the total. If the bars were heated in a coal furnace to 750°, and then transferred to the electric furnace, some 25 per cent. of the electrical power might be saved. If this heating were done by coal having a calorific power of 8,500, at a thermal efficiency of 25 per cent., there would be needed 40 grams of coal. The question is, therefore, the relative cost of $88 \div 0.75 = 117$ Calories delivered electrically, and 40 grams of coal. The former requires $117 \div 0.239 = 490$ kilowatt-seconds = 8.2 kilowatt-minutes = 0.14 kilowatt-hours. At \$10.00 per kilowatt-year (8,760 hours) this would cost $0.14 \times 0.114 = 0.016$ cents. At \$5.00 per metric ton the coal would cost $0.040 \times 0.5 = 0.020$ cent. Under such assumed conditions of cost of power and of coal the electrical heating, even up to 750°, would be the cheaper.

Problem 78.

In an induction electric furnace of 170 kilowatts capacity, 4.7 tons of steel is made per day by melting together cold-

washed pig iron and scrap iron, the melted steel carrying 350 Calories per kilogram.

Required:

(1) The electric energy in kilowatt hours required per ton of steel produced.

(2) The thermal efficiency of the furnace.

(3) If one-third the material used were put into the furnace melted, carrying 275 Calories per kilogram, what would be the production per day and the power required per ton of steel?

Solution:

(1) Energy for 4.7 tons = 170 kw-days.
Energy for 1.0 ton = 36.2 "
Energy for 1.0 ton = 0.10 kw-year
Energy for 1.0 ton = **869** kw-hours. (1)

(2) 1 kw-hour = $0.239 \times 60 \times 60$ = 860 Calories
869 kw-hours = 747,340 "
Heat in 1 ton of steel = $350 \times 1{,}000$ = 350,000 "

$$\text{Thermal efficiency} = \frac{350{,}000}{747{,}340} = 0.47 = \mathbf{47} \text{ per cent.} \quad (2)$$

(3) Heat in melted material used per kilogram of steel produced = $275 \times 1/3 = 92$ Calories.

Heat to be supplied by the current $350 - 92 = 258$ Calories.

Production per day under these conditions:

$$4.7 \times \frac{350}{258} = \mathbf{6.4} \text{ tons.} \quad (3)$$

Relative times for the heats = 1 to 0.74.

Energy required per ton = $170 \div 6.4$ = 26.6 kw-days.
= 0.07 kw-year.
= **638** kw-hours. (3)

Problem 79.

An electric steel furnace running at full heat, and containing about 2,500 kg. of steel, loses by radiation, etc., 250,000 Calories per hour; 2,500 kg. of melted pig iron is run into the hot furnace, carrying 250 Calories per kilogram, and it is treated with 500 kg. of iron ore, previously heated to 500° C., and 50

kg. of limestone added cold. The steel produced carries 400 Calories per kilogram and the slag 600 Calories. The operation lasts 1 hour. Assume the following composition of materials used and made:

Pig Iron.		*Iron Ore.*		*Limestone.*		*Steel.*	
Fe	96.656	Fe_2O_3	85.93	CaO	53.74	Fe	99.60
C	2.700	FeO	3.96	MgO	0.17	C	0.11
Si	0.600	SiO_2	5.50	SiO_2	3.14	Si	0.11
Mn	0.025	MnO	0.63	Fe_2O_3	0.18	Mn	0.15
S	0.007	Al_2O_3	0.76	Al_2O_3	0.32	S	0.02
P	0.012	CaO	2.23	P_2O_5	0.006	P	0.01
		MgO	0.97	S	0.001		

The bath was treated by the final addition of 10 kg. of cold ferro-manganese, carrying 80 manganese, 16 iron and 4 carbon. The steel obtained weighed 2,630 kg.

Required:

(1) A balance sheet of materials entering and leaving the furnace.

(2) The weight and percentage composition of the slag.

(3) A balance sheet of the heat received and distributed.

(4) The net power required to run the furnaces and the cost of power per ton of steel made, at $25.00 per kilowatt-year.

Balance Sheet.

Charges.		*Steel.*	*Slag.*		*Gases.*	
Pig Iron....(2500 Kg.)						
Fe	2416.4	2416.4	.....	.....	.....	.....
C	67.5	2.5	.....	.....	C	65.0
Si	15.0	2.9	SiO^2	24.9	.....	.....
Mn	0.6	.....	MnO	0.8	.....	.....
S	0.2	0.5	.....	.....	.....	.....
P	0.3	0.3	.....	.....	.....	.....
Ore.....(500 Kg.)						
Fe^2O^3	429.7	203.1	FeO	125.6	O	87.2
FeO	19.8	.....	FeO	19.8	.....	.....
SiO^2	27.5	.....	SiO^2	27.5	.....	.....
MnO	3.2	.....	MnO	3.2	.....	.....
Al^2O^3	3.8	.....	Al^2O^3	3.8	.....	.....
CaO	11.2	.....	CaO	11.2	.....	.....
MgO	4.8	.....	MgO	4.8	.....	.....

Limestone.....(50 Kg.)						
CaO.....	26.9	.....	CaO.....	26.9	.....	
MgO.....	0.1	.....	MgO.....	0.1	.....	
SiO^2.....	1.6	.....	SiO^2.....	1.6	.....	
Fe^2O^3.....	0.1	.....	FeO.....	0.1	.....	
Al^2O^3.....	0.2	.....	Al^2O^3.....	0.2	.....	
CO^2.....	21.2	.....	.....		CO_2.....	21.2
Ferro-manganese (10 Kg.)						
Fe.....	1.6	1.6	.....		.....	
C.....	0.4	0.4	.....		.....	
Mn.....	8.0	3.9	MnO.....	5.3	.....	
	3060.0	2631.6		255.8		173.4

(2) The slag contains:

			Per Cent.	
SiO^2.....	54.0	pounds	= 21.1	
Al^2O^3.....	4.0	"	= 1.5	
CaO.....	38.1	"	= 14.9	
MgO.....	4.9	"	= 1.9	
FeO.....	145.5	"	= 56.9	
MnO.....	9.3	"	= 3.6	
	255.8	"	= 99.9	(2)

Heat Available.

		Calories.
Electric current:		x
Oxidation of C to CO	65.0×2,430 =	157,950
Oxidation of CO to CO^2	0.9×2,430 =	2,190
Oxidation of Si to SiO^2	12.1×7,000 =	84,700
Oxidation of Mn to MnO	4.7×1,653 =	7,770
Formation of slag	22.6× 150 =	3,390
Heat in melted pig iron	2,500× 250 =	625,000
Heat in iron ore	500× 77 =	38,500
	Sum =	x+919,500

Heat Distribution.

		Calories
Heat in melted steel	2,630× 400 =	1,052,000
Heat in melted slag	256× 600 =	153,600
Reduction of Fe^2O^3 to FeO	386.7× 446 =	172,470

Reduction of FeO to Fe	$203.1 \times 1{,}173 =$	238,240
Separation of carbon from iron	$65 \times 705 =$	45,800
Heat in gas at 1,500°:		
$CO = 151.7$ kg. $= 120.4\ m^3 \times 0.32 \times 500$	$=$	19,260
$CO^2 = 1.4$ kg. $= 0.7\ m^3 \times 0.60 \times 500$	$=$	200
Loss by radiation, etc.	$=$	250,000
	Total $=$	1,931,570

Heat to be supplied by current:

$$x = 1{,}931{,}570 - 919{,}500 = 1{,}012{,}070 \text{ Calories.} \quad (3)$$

(4) One kilowatt furnishes per hour 860 Calories, therefore the power required to run the furnace is:

$$1{,}012{,}070 \div 860 = 1{,}177 \text{ kilowatts.} \quad (4)$$

At $25.00 per kilowatt-year a kilowatt-hour would cost

$$\$25.00 \div 8{,}760 = 0.2854 \text{ cents.}$$

And the power to run the furnace 1 hour would cost

$$0.002854 \times 1{,}177 = \$3.36.$$

And the cost per ton of steel:

$$\$3.36 \div 2.630 = \mathbf{\$1.32}.$$

Problem 80.

It is desired to design a plant for the electro-deposition of pure iron by the Burgess process (see Transactions American Electrochemical Society, Vol. V., p. 201). The desiderata and data are as follows:

Output, 25 metric tons per day.

Current density, 110 amps. per square meter.

Anodes, 0.75×0.5 meters immersed $\times 3$m.m. thick.

Cathodes, 0.75×0.5 meters immersed $\times 1$ m.m. thick at starting.

Cathodes to be run until deposit is 1.5 c.m. thick on each side.

Anodes run until 0.9 consumed.

Tanks, 1.00 meter deep, 0.6 m. wide, 2 m. long inside, filled to within 0.10 meter of top with electrolyte.

Working distance between anode and cathode 6 centimeters at starting.

Electrolyte contains 10 per cent. $FeSO^4$. $7H^2O$, and 5 per cent. $(NH^4)^2SO^4$, specific gravity 1.1, electrical resistivity 20 ohms per centimeter cube.

Voltage *drop* in connections and conducting rods 0.3 volt per tank.

Main conductors carry 2 amps. per m.m. square of section.

Net cost of electrical power, $25.00 per kilowatt-year.

Requirements:

(1) The number of anodes and cathodes per tank and the number of tanks in the plant and their arrangement.

(2) The weight of anodes and cathode sheets, increasing the weight of immersed part 10 per cent. Specific gravity of the rolled iron 7.9

(3) The weight of ferrous sulphate and ammonium sulphate required to start the plant.

(4) The drop of potential across the electrodes at starting and at the close of a deposition; the drop of potential per tank; the total voltage needed at starting the plant and when it is in regular operation.

(5) The cross sectional area of the main conductors.

(6) The time required to consume an anode plate, *i. e.*, in dissolving iron away equal to 0.9 of its weight.

(7) The time required to deposit a full cathode plate; specific gravity of the deposit 7.6

(8) The electric power required to run the plant and its cost per ton of iron deposited.

Solution:

(1) 110 amps. per square meter deposits per day:

$$0.00001036 \times 110 \times \frac{56}{2} \times 60 \times 60 \times 24 = 2{,}757 \text{ grams Fe.}$$

Therefore, depositing surface required:

$$25{,}000 \div 2{,}757 = 9{,}140 \text{ square meters.}$$

Since one cathode plate has a depositing area on both sides of $0.75 \times 0.5 \times 2 = 0.75$ square meter, the number of cathode plates required in the whole plant is:

$$9{,}140 \div 0.75 = 12{,}187$$

In one tank, if there are x cathodes and $x+1$ anodes, the thickness of these plates at starting is, in millimeters, $x+3$ $(x+1) = 4x+3$ m.m. The number of spaces between anodes and cathodes being $2x$, and each of these being 6 c.m. = 60 m m. at starting, the spaces are $120x$ m.m. The length of the tank being, inside, 2,000 m.m.:

$$124x+3 = 2,000$$

whence $$x = 16.1.$$

Each tank will therefore contain 16 cathodes and 17 anodes, at a distance apart, at starting of

$$\frac{2,000—16—3\ (17)}{2\ (16)} = 60.4 \text{ m.m.} = \mathbf{6.04} \text{ c.m.} \qquad (1)$$

Since we need 12,187 cathode plates we need

$$12,187 \div 16 = 761.7 \text{ tanks}$$

Which means that we would use **762** tanks. (1)

The arrangement of the tanks in series and groups of series can be best discussed when we know the voltage drop per tank, grouping them so as to absorb either 110 or 220 volts per series in one group.

(2) An anode sheet weighs:

$$75 \times 50 \times 0.3 \times 7.9 \times 1.1 = 9,776 \text{ grams,}$$

of which there is immersed 8,888 grams.
The 17 anodes per tank weigh altogether:

$$9.776 \times 17 = 166.2 \text{ kg.,}$$

and the 16 cathodes, which are one-third as thick:

$$3.259 \times 16 = 521.1 \text{ kg.}$$

In the whole plant, at starting, the weights will be:

Anode sheets	$166.2 \times 762 =$	**126,644** kg.
Cathode sheets	$52.1 \times 762 =$	**39,700** " (2)

(3) Volume of liquid in tank:

$$(1—0.1) \times 0.6 \times 2 = 1.08 \text{ cubic meters.}$$

Weight of solution per tank:	
$0.18 \times 1{,}000 \times 1.1$	= 1,188 kg.
Weight of dissolved salts:	
Copperas	= 118.8 "
Ammonium sulphate	= 59.4 "
Weight in the whole plant:	
Copperas	= **90.5** tons.
Ammonium sulphate	= **45.3** " (3)

(4) At starting the surface of the electrodes are 6.04 c.m. apart, and 110 amps. passes through each square meter of electrode surface; therefore, $110 \times 0.375 = 41.25$ amps. pass from each free side of each anode plate to the corresponding side of a cathode plate. Neglecting the small cross sectional area of electrolyte outside the plates, the resistance of each space would be

$$\frac{20 \times 6.04}{75 \times 50} = 0.322 \text{ ohms},$$

and the drop of voltage across two electrodes:

$$0.0322 \times 41.25 = \mathbf{1.33} \text{ volts}.$$

If we take into account the 5 c.m. free space at the sides of each electrode, and allow an equal amount as effective beneath, the cross-section of the electrolyte may be taken as

$$(75+5) \times (50+10) = 4{,}800 \text{ c.m}^2.,$$

and the resistance between two plates:

$$20 \times 6.04 \div 4.800 = 0.0252 \text{ ohms},$$

and the drop $0.0252 \times 41.25 = \mathbf{1.04}$ volts.

This value is the more probable one of the two.

At the close of a deposition, neglecting the decreased thickness of the thin anode plates, the working distance is decreased by one and a half centimeters, and the voltage drop between plates will then be:

$$\frac{20 \times 4.54}{4{,}800} \times 41.25 = \mathbf{0.78} \text{ volt}.$$

In both cases the voltage drop in contacts and conductors being 0.3 volt, the working voltage per tank will be:

	Volts.
At starting	**1.34**
At end	**1.08**
Average	**1.21**

The voltage needed at the generators can only be calculated when we assume a plan of grouping the 762 tanks. If we assume 110 volts to be desired at the generators, we could run 102 tanks in one series, which would give 7½ series. If we used 220 volts at the generators 2 series of 190 cells and 2 of 191 would absorb at starting 255 and 256 volts respectively, but when in regular running, with tanks in all stages of deposition, 205 and 206 volts. This would be a reasonable and practicable arrangement. In reality, at least one if not two additional tanks would be slipped into each series, for at least that number would be out of circuit continuously, being cleaned and made ready for re-starting.

(5) The amperes per tank would be:

$$0.75 \times 0.5 \times 2 \times 16 \times 110 = 1{,}320$$

And the area of the main conductors in each series:

$$1{,}320 \div 2 = 660 \text{ sq. m.m.} \qquad (5)$$

(6) The part of the anode sheet immersed weighs 8,888 grams, of which 0.9 is 8,000 grams, and if the anode is an intermediate one it is corroded on both sides, and receives, therefore, 85 amps. of current. This current dissolves, per second:

$$0.00001036 \times 28 \times 85 = 0\ 024657 \text{ grams.}$$

And therefore the anode sheet will last

$$8{,}000 \times 0.024657 = 324{,}000 \text{ seconds.}$$
$$= \quad 90 \text{ hours.} \qquad (6)$$

(7) The weight of deposit on both sides of a cathode plate is

$$75 \times 50 \times 2 \times 1.5 \times 7.6 = 85{,}500 \text{ grams.}$$

And the time required to deposit this, since it is deposited by 85 amps., is

$$85{,}500 \div 0.024657 = 3{,}467{,}600 \text{ seconds.}$$
$$= \mathbf{40} \text{ days } \mathbf{3} \text{ hours.} \qquad (8)$$

(8) Each series requires 1,320 amps. at 205 volts, or

$$1{,}320 \times 205 \div 1{,}000 = 270.6 \text{ kilowatts.}$$

The three series therefore require 812 kilowatts, which will cost

$$\$25.00 \times 812 \div 365.25 = \$55.68 \text{ per day.}$$

An average cost of power per ton of iron refined of

$$\$55.68 \div 25 = \$2.23. \qquad (8)$$

The other items of cost in a well conducted refinery will about equal this sum, making the total cost of refining about $4.50 per ton of pure iron. With cheap soft steel used as the raw material, there is a striking possibility of such a process being commercially practicable for furnishing one of the raw materials for producing the finest qualities of steel, the other raw material being washed pig metal of standard quality. We commend this possibility to the attention of the makers of fine steel.

APPENDIX TO PART II.

PROBLEMS FOR PRACTICE.

Problem 81.

A blast furnace will require 7000 cubic feet of cold air supplied per minute, and assuming that it will be provided with 5 tuyeres, and that the pressure in the main will be kept at 8 pounds per square inch, that the back pressure in the furnace will average 2 pounds per square inch, and that the coefficient of contraction of the jet, for a conical nozzle, is 0.92—

Required:

(1) The diameter of each nozzle.

Ans.: **3** inches.

Problem 82.

A blast-furnace charge is composed of the following ingredients, in percentage composition:

Ore		*Coal*		*Ash of Coal*		*Flux*	
Fe^2O^3	71.49	fixed C	90	SiO^2	48.00	CaO	52.83
SiO^2	15.73	ash	10	Al^2O^3	41.20	CO^2	41.51
Al^2O^3	4.21			Fe^2O^3	8.00	SiO^2	5.66
CaO	5.00			CaO	2.80		
MgO	3.57						

Per ton of pig iron there is used 1.5 tons of coal. Pig iron contains 94 per cent. Fe, and 2.8 per cent. Si, 99 per cent. of the iron in the charge goes into the pig iron. Quantivalent ratio of the slag, calling both Si and Al acids, 1.882.

Required, per ton of pig iron produced:

(1) The weight of ore charged. *Ans.*: **1.88** tons
(2) " " " flux " *Ans.*: **0.48** tons
(3) " " " slagproduced *Ans.*: **0.91** tons
(4) The percentage composition of the slag.

Ans.:

SiO^2	36.95 per cent.
Al^2O^3	15.56 "
CaO	38.79 "
MgO	7.40 "
FeO	1.30 "
	100.00 "

Problem 83.

The composition of the waste gases of a blast furnace is by weight (not by volume)

Nitrogen	55.40
Carbonous oxide	28.00
Carbonic oxide	16.50
Hydrogen	0.10

From analyses of the charges and products it is known that for every 100 kg. of pig-iron made 79.52 kg. of oxygen enters the gas from the solid charges and 15.5 kg. of carbon enters the gases from other sources than the fixed carbon of the fuel. The fuel contains 90 per cent. fixed carbon; the pig-iron contains 3 per cent. carbon. In 24 hours there is produced 41,400 kg. of pig-iron; the blowing engine works 23 hours. Assume blast dry.

Required:

(1) Per 100 kg. of pig iron, the weight of fuel charged.
Ans.: **114.4** kg.

(2) " " " " the carbon burned at the tuyeres.
Ans.: **87.4** kg.

(3) " " " " the carbon otherwise consumed.
Ans.: **12.6** kg.

(4) " " " " the weight of the gases.
Ans : **700** kg.

(5) " " " " the weight of the gases.
Ans.: **504** kg.

(6) The volume of blast received per minute.
Ans.: **117** m^3.

(7) The dimensions of the blast cylinder.
Ans.: $l = 1.5$ m, $d = 1.88$ m., **20** r.p.m.

Problem 84.

Four varieties of ore are used in a blast-furnace, containing by analysis:

	A	B	C	D
Fe	63.25	60.10	64.35	62.35
SiO^2	5.86	4.20	5.30	6.58
Al^2O^3	1.48	1.98	1.96	1.87
CaO	1.04	——	0.16	0.90
MgO	0.75	——	0.09	0.51
P	0.019	0.107	0.019	0.015

The flux, fuel and pig iron contained:

	Flux	*Fuel*	*Pig Iron*
SiO^2	5.46	5.64	Fe 95.24
Al^2O^3	1.53	3.74	Si 1.40
CaO	47.00	0.56	
MgO	3.60	0.60	
P	0.010	0.020	
		FeS 1.32	

The ores are mixed in the proportions $\frac{1}{3}$ A, $\frac{1}{3}$ B, $\frac{2}{3}$ C, $\frac{1}{9}$ D. A "round" of fuel consists of 12 barrows of coke containing 520 pounds per barrow. 1885 pounds of coke is used in producing a "ton" of 2300 pounds of pig-iron. Assume $\frac{9}{10}$ of the sulphur to go into the slag, and $\frac{9}{10}$ of the phosphorus to go into the pig-iron.

Required:

(1) A corrected fluxing table, showing for each substance (100 parts) the weights of ingredients furnished to the slag, the quantivalence of each element thus contributed, and the net available acid or basic quantivalence assuming the slag to be a bi-silicate, counting Si and Al as the acid elements in the slag.

(2) The weight of each ingredient of the burden per round of coke. *Ans.*: Ore **11,640** lb., flux **1090,** coke **6240.**

(3) The weight of slag produced per 2300 lbs. of pig-iron.

(4) The percentage composition of the slag.

(5) The percentage of S and P in the pig-iron.

Problem 85.

The flux used in a blast-furnace and the slag produced by its use have the following compositions:

Flux		*Slag*	
$CaCO^3$	80.36	CaO	29.0
$MgCO^3$	15.75	MgO	4.8
SiO^2	3.00	SiO^2	53.4
H^2O	0.89	Al^2O^3	9.0
		FeO	2.6
		Na^2O	1.2

Per 100 kg. of pig iron produced there is used 28.7 kg. of flux. and there is made 50.15 kg. of slag.

Required:

(1) The quantivalent ratio of the slag.

Ans.: **2.96**

(2) How much flux would be needed to produce a uni-silicate slag. *Ans.*: **105** kg.

(3) What would be the weight of this slag.

Ans.: **93** kg.

(4) What would be its percentage composition; check the quantivalent ratio from this composition.

Problem 86.

A blast furnace works on the following materials:

Ore		*Coke*		*Flux*		*Pig Iron*		*Gases*	
Fe^2O^3	85	Fixed C	87	CaO	52.50	Fe	94.8	CO	28.41
SiO^2	9	SiO^2	6	SiO^2	6.25	Si	1.4	CO^2	10.85
Al^2O^3	1	Al^2O^3	5	CO^2	41.25	C	3.8	N^2	60.78
CaO	2.8	H^2O	2						
H^2O	2.2								

100 kg. of coke and 160 kg. of ore are used per 100 kg. of pig-iron produced.

Required: (1) The weight of flux charged, per 100 of coke, to make a slag with the quantivalent ratio:

$$\frac{\text{Quant. Si} + \text{Quant. Al}}{\text{Quant. Ca}} = 1.75.$$

Ans.: **39.1** kg.

(2) The weight of carbon burned at the tuyeres per 100 of pig-iron. *Ans.*: **70.1** kg.

(3) The weight of carbon consumed above the tuyeres per 100 of pig-iron. *Ans.*: **13.1** kg.

Problem 87.

The blast-furnace of preceding problem has 7 tuyeres, each 5 inches in diameter. Temperature of blast in blast main 819°, indicated pressure on blast-main gauge 22.08 lbs. per sq. inch, the back pressure in the furnace in the region of the tuyeres is 3.69 lbs. per sq. inch. The air jet contracts in issuing until the coefficient of contraction of area of the jet—μ—is 0.9.

Required: (1) The actual temperature of the blast entering the furnace, assuming it to be cooled only by expansion. Assume the mean specific heat of air under the above conditions as 0.40 (oz. cal. per cubic foot or Cal. per cubic meter).

Ans.: **743°**

(2) The volume of blast per minute received by the furnace, at standard conditions of measurement. *Ans.*: **48,400** ft^3.

Problem 88.

Taking the calculated data of Problems 86 and 87, and combining them, how many tons of pig-iron, at 2240 lbs. per ton, are produced per day, assuming the blast to be on the furnace 23 hours 30 minutes? *Ans.*: **700** tons.

Problem 89.

A blast furnace makes 330,000 kg. of pig iron in 24 hours. The blowing engine runs 1400 minutes per day; 3 cylinders, double acting, 2 m. diameter by 2 m. stroke, piston rod 0.1 m. diameter and passing through one end of the cylinder only; 40 strokes per minute. Temperature in engine room 27.3°; assume air dry.

Charges per 100 kg. of pig iron: Ore 155.0, flux 45.2, coke 84.0. Ore contains 62 per cent. of Fe, as Fe^2O^3, 5 per cent. H^2O and the rest SiO^2. The flux is 3 per cent. SiO^2 and the rest $CaCO^3$. The coke contains 89 per cent. fixed carbon, 1 per cent. H^2O and the rest half SiO^2 and half Al^2O^3. The pig-iron carries 3.5 carbon, 1 silicon, 94.6 per cent. iron. The waste gases contain 2.3 volumes of CO to 1 volume of CO^2. Assume all the oxygen in the CO and CO^2 to come from the blast. reduction of Fe^2O^3 and SiO^2, and the CO^2 of the flux.

Required:

(1) The weight of carbon burned at the tuyeres, per 100 kg. of pig-iron produced. *Ans.*: **57.8** kg.

(2) The weight of carbon burned above the tuyeres, in direct reduction, per 100 of pig-iron. *Ans.*: **13.5** kg.

(3) The volume of blast, at standard conditions, received by the furnace per minute. *Ans.*: **608.5** m^3

(4) The same, per ton of pig-iron. *Ans.*: **2582** m^3

(5) The efficiency of the blowing plant, *i.e.*, the ratio of air received to the piston displacement. *Ans.*: **88.9** per cent.

Problem 90.

A blast-furnace produces 300 metric tons of pig-iron per day, and is charged, per 100 kg. of pig-iron, with

156 kg. iron ore
50 " limestone
90 " coke

The percentage compositions of these materials and of the pig-iron and gases produced are:

Ore		*Limestone*		*Coke*		*Pig Iron*		*Gases*
Fe^2O^3	85	CaO	51.66	Fixed C	88	Fe	94.00	CO 26.50
SiO^2	8	MgO	2.50	SiO^2	8	Si	2.10	CO^2 13.25
Al^2O^3	4	SiO^2	2.50	FeS	2	C	3.75	N^2 60.25
H^2O	3	CO^2	43.34	H^2O	2	S	0.10	

Required:

(1) The volume of gas, measured dry, at 0° and 760 m.m. pressure, produced per 100 kg. of pig-iron made. *Ans.*: **379** m^3

(2) The volume of blast, assumed dry and at 0° and 760 m.m., received per 100 kg. of pig-iron made. *Ans.*: **288** m^3

(3) The weight of carbon consumed by the blast, at the tuyeres, per 100 kg. of pig-iron made. *Ans.*: **66** kg.

(4) The weight and percentage composition of the slag. *Ans.*: **49** kg.

Composition: SiO^2 32.6, Al^2O^3 12.4, CaO 49.3, MgO 2.4, FeO 1.2, CaS 2.4.

(5) The horse-power producible from one-half of the gases, assuming them used in gas-engines at 25 per cent. net thermo-mechanical efficiency. *Ans.*: **7570** h.p.

Problem 91.

A blast-furnace makes 300 metric tons of pig-iron daily, producing per 100 kg. of pig iron made 464.5 m^3 of gas of the

following composition: CO 24, CO^2 12, N^2 64, and using 352.5 m^3 of blast, at 700° C. The blowing engines consume 1,000 indicated horse-power, the lift and pumps 150 h.p. The blast (assumed dry at 0°) is heated to 700° in fire-brick stoves, at an efficiency of 50% on the heat of combustion of the gas used in them.

Required:

(1) The proportion of the gas made by the furnace required to be used by the stoves. *Ans.*: **46.6** per cent.

(2) The rest of the gas being burned under boilers, and just raising the power required by the furnace, what is the net thermo-mechanical efficiency of the boilers and engines together? *Ans.*: **3.2** per cent.

(3) If these gases were used in gas engines at an efficiency of 25 per cent., what surplus power would the blast-furnace produce above its own requirements? *Ans.*: **7830** horse-power.

Problem 92.

An Alabama blast furnace uses and produces materials of the following compositions:

Ore		*Dolomite*		*Coke*		*Pig Iron*	
Fe^2O^3	72.85	CaO	30.24	C	86.00	Fe	93.54
SiO^2	9.00	MgO	20.48	SiO^2	4.00	C	3.50
Al^2O^3	3.75	Fe^2O^3	0.50	Al^2O^3	2.00	Si	2.25
CaO	0 75	Al^2O^3	0.50	Fe^2O^3	2.00	S	0.06
P^2O^5	0.90	SiO^2	2.00	S	1.00	P	0.65
SO^3	0.25	CO^2	46.28	H^2O	5.00		
CO^2	0.60						
H^2O	11.90						

Assume: Burden = 2.00 (*i.e.*, ore plus dolomite = twice coke). All the iron in the charge reduced into the pig iron.

Sulphur not in pig iron goes into slag as CaS.

Phosphorus not in pig iron goes into slag as P^2O^5.

Slag to contain 34.00 per cent. SiO^2.

Eighty-nine per cent. of the fixed carbon of the coke will be consumed at the tuyeres, by dry blast.

Required: A balance sheet of materials entering and leaving the furnace.

Solution: [N.B.—Let x = ore used, y = dolomite, then $\frac{x+y}{2}$ = coke, and the balance sheet thus constructed leads easily to a solution conforming to above conditions.]

BALANCE SHEET (per 1000 of pig iron).

Charges		*Pig Iron*		*Slag*		*Gases*	
Ore	**1792**						
Fe^2O^3	1305.5	Fe	913.9			O	391.6
SiO^2	161.3	Si	22.5	SiO^2	113.1	O	25.7
Ol^2O^3	67.2			Al^2O^3	67.2		
CaO	13.4			Ca	1.5	O	0.6
				CaO	11.3		
P^2O^5	16.1	P	6.5	P^2O^5	1.3	O	8.4
SO^3	4.5	S	0.6	S	1.2		
CO^2	10.8					CO^2	10.8
H^2O	213.2					H^2O	213.2
Flux	**411**						
CaO	124.3			Ca	13.8	O	5.5
				CaO	105.0		
MgO	84.2			MgO	84.2		
Fe^2O^3	2.1	Fe	1.5			O	0.6
Al^2O^3	2.1			Al^2O^3	2.1		
SiO^2	8.2			SiO^2	8.2		
CO^2	190.2					CO^2	190.2
Coke	**1101**						
C	946.9	C	35.0			C	911.9
SiO^2	44.0			SiO^2	44.0		
Al^2O^3	22.0			Al^2O^3	22.0		
Fe^2O^3	22.0	Fe	15.4			O	6.6
S	11.0			S	11.0		
H^2O	55.1					H^2O	55.1
Blast	**4004**						
O^2	924.					O	924.0
N^2	3080.					N	3080.0
	7308.		1000.0		485.9		5824.2

Charges		*Slag*			
Coke	1000	SiO^2	34.0%	CaS	5.7
Ore	1628	Al^2O^3	18.8%	P^2O^5	0.3
Flux	373	CaO	23.9%		100.2
Pig Iron	908	MgO	17.5%		

Problem 93.

A foundry cupola melts 6,000 kg. of pig iron per hour, using 480 kg. of coke containing 85 per cent. fixed carbon. Average composition of issuing gases, by volume, N^2 75, CO^2 16, CO 4. Some Fe, Mn and Si are oxidized, forming the silicate Fe^5 Mn SiO^8. No carbon is oxidized out of or absorbed by the pig-iron. Assume the blast dry and neglect the ash of the coke and corrosion from the lining.

Requirements:

(1) The volume of blast received by the cupola per minute.
Ans.: **59.7** m^3

(2) The percentage loss in weight of the pig-iron, assuming it to lose only Fe, Mn and Si. *Ans.*: **4.74** per cent.

(3) The proportion of the whole heat generated which is due to the oxidation of carbon and to the oxidation of the pig-iron.
Ans.: **84.5** and **15.5** per cent.

Problem 94.

Dichmann, in *Stahl und Eisen*, 1 December, 1905, gives the following data respecting the Monell open-hearth operation, as practised by him.

Charge: 1000 kg. limestone, CaO 54.1, SiO^2 1.65, MgO 0.68.
3276 " hematite ore, Fe^2O^3 95.0, SiO^2 3.7.

These were put on a basic hearth and heated nearly to melting. There was then run upon them 20,300 kg. of melted pig-iron. Starting at 2.30 P.M., the subsequent analyses showed:

	Metal				*Slag*				
P.M.	C	Si	P	Mn	FeO	Fe^2O^3	Mn	P^2O^5	SiO^2
2.30	4.61	0.84	0.15	2.20					
3.00	4.56	0.19	0.05	0.45	47.88	6.10	15.22	2.36	17.68
5.40	1.47	0.05	0.03	0.63	10.36	3.23	12.67	2.35	23.00
5.45	(819 kg. more ore added)								
6.15	0.43	0.05	0.03	0.49	11.44	2.37	12.04	2.03	22.90

Required:

(1) The weight of iron reduced into the bath during the slag-forming period—2.30 to 3.00 P.M.
Ans.: **1219** kg. = **56%** of the iron in the ore.

(2) The weight of iron reduced into the bath during the boil—3.00 to 5.40 P.M.

Ans.: 705 kg. = 32.4% of the iron in the ore.

(3) The weight of iron reduced from the additional ore added —5.40 to 6.15 P M

Ans.: 509 kg. = 93% of the iron in the ore added.

(4) The proportion of oxidation produced by the ore and by the furnace gases in each of these periods.

Ans.: 1st period **100** and **0.**
2d " **30** and **70.**
3d " **73** and **27.**

Problem 95.

A Bessemer converter is charged with 10,000 kg. of pig-iron, from which is oxidized

Si	2.8 per cent.	
C	3.3 "	1/5 to CO^2
Fe	1.12 "	

Length of blow 15 minutes, no free oxygen escapes from the converter. Temperature in engine room 0°, barometer 760 m.m., mean pressure on piston of blowing cylinder during the stroke 1 kg. per sq. centimeter. No moisture in the air. Assume a coefficient of delivery of 0.60.

Required:

(1) The volume of blast received per minute.

Ans.: **196** m^3

(2) The dimensions and speed of the blowing cylinder.

Ans.: *d* **2.4** m., *l* **2** m., **18** r.p.m.

(3) The horse-power exerted by the blowing cylinder.

Ans.: **727** h.p.

(4) If the speed of the blowing cylinder is kept constant, but the temperature in the engine room becomes 30° and saturated with moisture, how much longer will the blow last?

Ans.: **46** seconds.

Problem 96.

A Bessemer converter contains 10,000 kg. of pig-iron, from which there is oxidized by the blast: Si 1, Fe 2, C as CO^2 0.7, C as CO 2.8 per cent., while no free oxygen or H^2O vapor escapes

from the converter. The blowing engines have a piston displacement of 326.5 m^3 per minute. The air in the engine room is at 27.3°, barometer 741 m.m., air saturated with moisture. The blow lasts 9 minutes 10 seconds, up to the end of the boil.

Required:

(1) The coefficient of useful delivery of the blowing cylinders and conduits. *Ans.*: **66** per cent.

(2) The average composition of the gases produced.

Ans.: CO 5.18, CO^2 20.73, H^2 3.38, N^2 70.80 per cent.

Problem 97.

The gases from a Bessemer converter had the following average composition during the slag-forming period and the boil, respectively:

	First 3 *minutes.*	*Last* 2 *minutes.*
O^2	0.6	0.1
CO^2	8.4	4.3
CO	5.2	26.1
H^2	0.6	0.6
N^2	85.2	68.9

Duration of blow 5 minutes. Weight of charge 2500 kg. Weight of carbon oxidized 3.9 per cent. of the weight of the charge. Assume the blast constant per minute throughout, and that the composition of the slag formed from the Fe, Mn and Si, oxidized is Fe Mn Si^2O^6. Neglect the moisture of the blast.

Required:

(1) The volume of the blast per minute. *Ans.*: **168.5** m^3

(2) The proportion of the total carbon oxidized passing off as CO^2. *Ans.*: **30.9** per cent.

(3) The percentage loss in weight of the charge from the oxidation of its ingredients. *Ans.*: **9.30** per cent.

Problem 98.

A Bessemer converter is charged with 8000 kg. of pig-iron. The slag-forming period lasts 6′ 20″, the boil 4′ 10″. At the end of the boil 800 kg. of spiegeleisen is added, and the converter momentarily turned up. The steel ingots obtained weigh 7900 kg. Hydrogen in gases comes from moisture in the blast.

Temperature of air in engine room 30° C., barometer 760 m.m. Assume blast constant per minute. Blast cylinder 1.5 m. internal diameter, 2 m. stroke, double acting, 90 strokes per minute, piston rod through both ends, diameter 0.15 m. Effective pressure of the blast, 2 atmospheres.

Analyses:

	Pig Iron	*End of 1st period*	*End of 2d period*	*Spiegel*	*Steel*
C	4.00	2.63	0.04	5.00	0.49
Si	2.00	0.26	0.03	3.00	0.10
Mn	1.40	0.42	0.01	15.00	0.78
P	0.05	0.05	0.06	0.12	0.06
S	0.05	0.05	0.06	——	0.05
Fe	92.50	96.59	99.80	76.88	98.52

Average composition of gases:

	In 1st period	*In 2d period*
CO	7.19	27.45
CO^2	7.19	2.60
O^2	2.60	——
H^2	2.81	2.36
N^2	80.21	67.59

Final Slag	
SiO^2	48.62
MnO	21.72
FeO	29.66

Required:

(1) A balance sheet, showing constituents of the bath at each stage of the blow.

(2) The volume of blast per minute, at the engine room temperature; the weight of blast per ton of pig-iron treated.

(3) The relative volumes of gas issuing per minute in each period.

(4) The proportion of the total carbon burned in the blow which is burned to CO and CO^2.

(5) The proportions of the carbon, silicon and manganese of the spiegeleisen lost during re-carbonization. Express these also as percentages of the weight of steel produced

(6) The total weight of the slag; the weight of silica corroded from the lining.

(7) The volume efficiency of delivery of the blowing engine.

(8) The net effective horse-power of the blowing cylinder.

Solution:

(1) BALANCE SHEET

	Pig Iron	*Loss*	*End* 1*st period*	*Loss*	*End* 2*d period*	*Spiegel*	*Loss*	*Steel*
C	320	120	200	197	3	40	4	39
Si	160	140	20	18	2	24	18	8
Mn	112	80	32	31	1	120	59	62
P	4	—	4	0	4	1	0	5
S	4	—	4	0	4	0	0	4
Fe	7400	60	7340	124	7216	615	49	7782
Total	8000	400	7600	370	7230	800	130	7900

(2) Volume received by converter per minute at 30°: **287** m^3

Weight per ton of pig-iron treated: **436** kg.

(3) Relative volumes of gases per minute: **1** to **1.20**

(4) Proportion of carbon burned to CO: **75.7** per cent.

(5) Loss in per cent. of spiegel: in per cent. of steel

C	0.5	0.05
Si	2.3	0.23
Mn	7.4	0.75

(6) Weight of slag: **1005** kg. Loss of lining: **112** kg.

(7) Efficiency of delivery = **82.5** per cent.

(8) Net effective horse-power = **900**; gross, **1000.**

Problem 99.

Ten metric tons (10,000 kg.) of pig-iron is charged into a basic lined (Thomas) Bessemer converter, and blown 12 minutes. The lining is burnt dolomite, composition practically CaO, MgO. Analyses showed:

Pig Iron		*Metal at end of blow*		*Slag*	
C	3.05	C	0.1687	SiO^2	5.98
Mn	0.41	Mn	0.0973	MnO	1.39
Si	0.83	Si	———	CaS	2.49
S	0.33	S	0.0540	P^2O^5	10.08
P	1.37	P	0.0650	FeO	7.14
Fe	94.01	Fe	99.6150	Fe^2O^3	1.20
				CaO	67.05
				MgO	4.67

Assume all the Fe, Si and Mn oxidized to be removed in the first period, all the carbon in the second, $\frac{1}{5}$ to CO^2 and $\frac{4}{5}$ to CO, and all the P and S in the third period, and no free oxygen to escape from the converter.

Requirements:

(1) The weight of slag produced. *Ans.*: **2975** kg.
(2) " " " steel " *Ans.*: **9250** kg.
(3) " " " lining corroded away during the blow. *Ans.*: **333** kg.
(4) " " " lime added during the blow. *Ans.*: **1858** kg.
(5) The duration of each period, assumed as sharply defined. *Ans.*: **2′ 27″, 6′ 50″, 2′ 43″.**

Problem 100.

In a basic-lined Bessemer converter, there is oxidized during the blow:

Silicon	0.84 per cent.	
Carbon	3.00 "	1/5 to CO^2
Phosphorus	1.86 "	
Manganese	0.55 "	
Iron	2.80 "	

Bath weighs at starting 8000 kg., blow lasts 18 minutes, no free oxygen escapes from the converter. Effective pressure of the blast 1.5 atmospheres, outside air at 0° and 760 m.m.

Requirements:

(1) The volume of the blast per minute. *Ans.*: **134** m^3
(2) The net horse-power of the blowing engine. *Ans.*: **313** h.p.
(3) If the slag has the formula: 3 $Ca^4P^2O^9$. $MnFe^5Ca^{12}$ Si^3O^{24}, how much lime must be added during the blow and what is the weight and percentage composition of the slag?

Ans.: **1075** kg. CaO
1905 kg. slag.

P^2O^5	17.89 per cent.
SiO^2	7.56 "
CaO	56.46 "
MnO	2.98 "
FeO	15.11 "

PART III.

THE METALS OTHER THAN IRON.

(NON-FERROUS METALS.)

CHAPTER I.

THE METALLURGY OF COPPER.

Roasting and Smelting Copper Ores.

The facts with regard to the metallurgy of copper may be found in condensed form, very clearly stated, in Schnabel's " Handbook of Metallurgy," Vol. I; they may be found discussed at greater length in Dr. Peters' " Modern Copper Smelting " and " Principles of Copper Smelting," in Eissler's " Hydrometallurgy of Copper," and in Ulke's " Modern Electrolytic Copper Refining." *In the following presentation it will be possible to merely enumerate the different processes concerned, the principles embodied in each and the methods of calculating quantitatively the nature of the reactions involved.

The chief ore of copper is chalcopyrite, $CuFeS^2$ which contains when pure approximately 30 per cent iron and 35 per cent each of copper and sulphur. It is most frequently found mixed with silica, SiO^2, as gangue, although various other gangue materials are sometimes present. This mineral is fusible, and if it were merely melted out of the enclosing rock, in an atmosphere which did not act upon it, it would simply lose one-fourth of its sulphur and melt to a fluid double sulphide of iron and copper, according to the following reaction:

$$2CuFeS^2 = Cu^2S.2FeS + S.$$

The melted sulphide of copper and iron resulting is called " matte," and, in fact, any mixture of Cu^2S and FeS in any proportions is called matte, and in practice may contain small quantities of PbS, ZnS, BaS, NiS, As, Sb, Te and even of Fe^3O^4, which is slightly soluble in these fused sulphides. In the majority of cases the matte is practically near enough to a mixture of Cu^2S and FeS to regard it as containing only those two substances.

*More recently, in Prof. H. O. Hofman's splendid treatise on "The Metallurgy of Copper."

Since the first operation in the extraction of copper from its usual sulphide ores is invariably the concentration to matte, we will first study the composition of this substance. Assuming matte to consist of Cu^2S and FeS in varying proportions, we may note that if it is all Cu^2S it contains $2 \times 63.6 = 127.2$ parts of copper to 32 parts of sulphur, or practically 4 copper to 1 sulphur, or is 80 per cent copper. For every 1.0 per cent of copper sulphide present there is, therefore, 0.8 per cent of copper in the matte; and, conversely, for every 1 per cent of copper in the matte there is 1.25 per cent of copper sulphide in it. The rest of the matte being iron sulphide, which contains 56 parts iron to 32 sulphur, it can be seen that the per cent of iron can be calculated for any per cent of copper; in fact, the per cent of copper fixes both that of iron and sulphur.

Illustration: A matte contains 40 per cent of copper. How much iron and sulphur does it contain? How much copper sulphide and iron sulphide?

40 per cent copper	$= 40 \times 5/4$	= 50 per cent	Cu^2S.
	100—50	= 50 "	FeS.
50 per cent FeS	$= 50 \times 56 \div 88$	= 31.8 "	Fe.
	100—(40+31.8)	= 28.2 "	S.

We may generalize this solution and say that if X represents the percentage of copper in a matte, that the composition of the matte is as follows:

Per cent of copper	= X
Per cent of Cu^2S	= 1.25 X
Per cent of FeS	= 100 − 1.25 X
Per cent of Fe = (100 − 1.25 X) 56/88	= 63.6 − 0.795 X
Per cent of S = 100 − X − Fe	= 36.4 − 0.205 X

Similarly, if Y represents the percentage of iron in a matte its composition is:

Per cent of Fe	= Y
Per cent of FeS	= 1.57 Y
Per cent of Cu^2S	= 100 − 1.57 Y
Per cent of Cu	= 80 − 1.26 Y
Per cent of S	= 20 + 0.26 Y

Finally, if Z represents the percentage of sulphur in a matte its composition is:

Per cent of S	= Z
Per cent of Fe	= 3.89 Z − 77.8
Per cent of Cu	= 177.8 − 4.89 Z
Per cent of FeS	= 6.11 Z − 122.3
Per cent of Cu^2S	= 222.3 − 6.11 Z

The following tables may then be drawn up, and will be found useful for reference:

Percentages.

Cu.	*Fe.*	*S.*	*Cu^2S.*	*FeS.*
80	0.0	20.0	100.0	0.0
75	4.0	21.0	93.8	6.2
70	8.0	22.0	87.5	12.5
65	12.0	23.0	81.3	18.7
60	15.9	24.1	75.0	25.0
55	19.9	25.1	68.8	31.2
50	23.9	26.1	62.5	37.5
45	27.9	27.1	56.3	43.7
40	31.8	28.2	50.0	50.0
35	35.8	29.2	43.8	56.2
30	39.8	30.2	37.5	62.5
25	43.8	31.2	31.3	68.7
20	47.7	32.3	25.0	75.0
15	51.7	33.3	18.8	81.2
10	55.7	34.3	12.5	87.5
5	59.7	35.3	6.3	93.7
0	63.6	36.4	0.0	100.0

For regular use in a smelting works it is easy to calculate a table similar to the above for every one per cent of copper, and keep it under a glass cover for constant reference. Or, if preferred, a large piece of cross-section paper can be taken, and a diagram prepared with the percentages of copper as abscissas, from 0 to 80, and with ordinates running up to 100. A line drawn from an ordinate 36.4 at abscissa 0 to ordinate 20 on abscissa 80, will represent the sulphur content; a line from ordinate 63.6 on abscissa 0 to ordinate 0 on abscissa 80,

will represent the iron content; a line from 0 to ordinate 100 on abscissa 80 will represent the Cu^2S content; and a line from ordinate 100 on abscissa 0 to ordinate 0 on abscissa 80 will represent FeS content.

It has been already shown that if a chalcopyrite ore were smelted down, as in a shaft furnace, to a matte, that about a 35 per cent matte is as rich as could be made by simple fusion. In fact, a much poorer matte would usually result, because chalcopyrite is often accompanied by pyrite, FeS^2, which on simple heating becomes FeS, and thus dilutes the matte still further.

Illustration: A chalcopyrite copper ore contains 30 per cent by weight of chalcopyrite and 25 per cent of iron pyrite. What grade of matte would result from a simple fusion of this ore, without roasting, in a reducing atmosphere?

Thirty per cent $CuFeS^2$ contains:

$30 \times 160 \div 368$	= 13	per cent	Cu^2S.
$30 \times 176 \div 368$	= 14	"	FeS.
25 per cent of FeS^2 will produce			
$25 \times 88 \div 120$	= 18	"	FeS.
Total matte	= 45	"	of the ore.

Composition of matte:

Cu^2S = 29 per cent = 23 per cent copper.
FeS = 71 "

It is thus seen that the presence of iron pyrites in the ore tends to lower the grade of the matte produced.

The essential principle of the metallurgy of copper is now before us. It is this fact: that if some of the sulphur in the ore be first removed by roasting, and this operation be followed by smelting, the copper will first take enough of the sulphur to form Cu^2S, and then what sulphur is left over will form FeS. The amount of FeS which will accompany the Cu^2S into the matte is entirely a question of how much sulphur is left to combine with iron after all the copper has been satisfied, and this amount of sulphur can be exactly controlled by the preliminary roasting.

Illustration: Taking the ore mentioned in the previous illustration, containing 30 per cent of chalcopyrite (= 10.4 per cent

of copper) and 25 per cent of iron pyrites, what per cent of sulphur does it contain, and what would be the quality of the matte produced by fusion in a reducing atmosphere if the sulphur were previously roasted down to ½ or ¼ or ⅛ of its original amount?

Sulphur in 30 per cent chalcopyrite:
$30 \times 128 \div 368$ = 10.5 per cent.
Sulphur in 25 per cent pyrites:
$25 \times 64 \div 120$ = 13.3 "
Total = 23.8 "

If the sulphur were reduced to ½, ¼ or ⅛ its original amount there would remain, out of the 23.8 per cent, either 11.9, 5.95 or 2.97 parts of sulphur per 100 of original ore; *i.e.*, per 10.4 parts of the copper. The 10.4 of copper requires 2.6 of sulphur to form Cu^2S, leaving the following amounts of sulphur in excess to form FeS:

Sulphur left in ore	11.90	5.95	2.97
Sulphur needed for Cu^2S	2.60	2.60	2 60
Sulphur left to form FeS	9.30	3.35	0.37
FeS which will be formed	25.61	9.21	1.02
Cu^2S formed	13.00	13.00	13.00
Matte formed	38.61	22.21	14.02
Per cent of Cu in matte	27.0	46.8	74.2

It is thus evident that the degree of the previous roasting determines absolutely the quality or grade of the matte formed on the subsequent smelting.

It can be readily seen that since partial roasting virtually oxidizes a portion or fraction of the ore, that it is the practical equivalent of roasting if we can get oxide ore to mix with sulphide ore. The raw oxide ore acts exactly as so much roasted ore, and thus enriches the matte on subsequent smelting.

Illustration: What proportion of a cuprite (copper oxide) ore, free from sulphur and containing 28 per cent of copper, can be mixed with the chalcopyrite ore of the previous illustrations, to produce a matte on subsequent reducing smelting containing 50 per cent of copper?

One hundred parts of the chalcopyrite ore contain 10.4 parts Cu, 20.8 parts Fe, 23.8 parts S.

The sulphur, however, is not all available for making matte, because one-fourth of the sulphur in chalcopyrite and one-half that in pyrite is given off by simple heating. There would be lost, therefore, and not available for matte, sulphur as follows:

S in chalcopyrite	$10.5 \times \frac{1}{4}$	=	2.6	not available.
S in pyrite	$13.3 \times \frac{1}{2}$	=	6.7	" "
			9.3	" "

Available sulphur $= 23.8 - 9.3 = 14.5$ parts per 100 of ore.

In a 50 per cent matte there is (see previous table) 26.1 per cent of sulphur; 14.5 parts of sulphur available for matte is therefore capable of producing $14.5 \div 0\,261 = 55.5$ parts of 50 per cent matte, which would contain 27.75 parts of copper. But there is only 10.4 of copper in the chalcopyrite ore, leaving therefore 16.35 of copper to be supplied by the cuprite ore, and therefore capable of taking up $16.35 \div 0.28 = 58$ parts of the oxide ore per 100 of the sulphide ore. A mixture of 100 of the sulphide ore and 58 parts of the oxide ore would therefore smelt down in a reducing atmosphere to a 50 per cent matte.

We have carefully specified a reducing atmosphere as the condition for smelting down to produce the calculated results, because under these conditions the oxygen of the roasted ore or of the raw oxide ore added cannot combine with the sulphur of the ore and go off as SO^2, but is taken up by the carbon or CO in the smelting furnace. In smelting in a shaft furnace with carbon as fuel these conditions exist, and the sulphur in the charge can be counted on as practically all forming matte. If the smelting is done in a reverberatory furnace, with a neutral atmosphere, much sulphur will be removed from the charge by the oxygen of the roasted ore or of the raw ore added, and a richer matte results. The reactions of this elimination of sulphur are mostly

$$Cu^2S + 2CuO = 4Cu + SO^2$$
$$Cu^2S + 2Cu^2O = 6Cu + SO^2$$

On an average, a matte 10 per cent richer in copper will be obtained from a given roasted ore by smelting it down in a reverberatory furnace, where these reactions between sulphide

and oxide of copper can occur, than in shaft furnace smelting with coke, in which the oxygen of the charge is taken up by the carbon.

There is a third variety of smelting which is in reality a combined roasting and smelting-down operation. We refer to what is called pyritic smelting, where a sulphide ore is roasted in a blast of air so rapidly that the heat generated melts down the charge and produces a concentrated matte. This operation is done on pure sulphides, however, without preliminary roasting, and will be subsequently discussed by itself.

The Roasting Operation.

When an ore is roasted it loses some sulphur and takes up oxygen. The roasted ore will therefore have a different weight from the unroasted ore. Thus:

100 parts of Cu^2S become	90.0	parts of	Cu^2O.
100 parts of Cu^2S become	100.0	"	CuO.
100 parts of Cu^2S become	100.0	"	$CuSO^4$
	50.0	"	CuO.
100 parts of FeS^2 become	64.5	"	Fe^3O^4
100 parts of FeS^2 become	66.7	"	Fe^2O^3
100 parts of FeS^2 become	126.7	"	$FeSO^4$

Problem 101.

A pyritous copper ore from Ely, Vt. (see Peters' "Modern Copper Smelting," p. 133), contained before and after roasting, in percentages:

	Before.	*After.*
Sulphur	32.6	7.4
Copper	8.2	9.1

The condition of the copper in the roasted sample was determined as

	Per Cent
Copper as $CuSO^4$	1.3
Copper as CuO	2.1
Copper as Cu^2S	5.7

Required:

(1) The weight of roasted ore per 100 of raw ore.

(2) The proportion of the sulphur removed by roasting.

(3) The grade of matte which would be formed by smelting down in a reducing atmosphere in a shaft furnace.

(4) The grade of matte which would be formed by smelting down in a neutral atmosphere in a reverberatory furnace.

Solution:

(1) Since no copper is lost, there will be produced per 100 of raw ore:

$$100 \times \frac{8.2}{9.1} = \mathbf{90.1} \text{ of roasted ore.} \qquad (1)$$

	Parts.
(2) Sulphur in 100 of raw ore	= 32.6
Sulphur in 90.1 of roasted ore = 90.1×0.074	= 6.7
Sulphur eliminated	= 25.9

Proportion removed:

$$\frac{25.9}{32.6} = 0.794 = \mathbf{79.4} \text{ per cent.} \qquad (2)$$

(3) Per 100 of roasted ore we have:

	Kg.
Sulphur to form $Cu^2S = 9.1 \times 0.25$	= 2.3
Sulphur to form FeS = 7.4 − 2.3	= 5.1
FeS formed = $5.1 \times 88/32$	= 14.0
Cu^2S	= 11.4
Matte formed	= 25.4

$$\text{Per cent of copper} = \frac{9.1}{25.4} = 0.358 = \mathbf{35.8} \text{ per cent.} \qquad (3)$$

(4) In

$$CuSO^4 + Cu^2S = 3Cu + 2SO^2$$

every 1 part of copper as $CuSO^4$ reduces two parts of copper as Cu^2S, and causes the elimination as gas of 1 part of sulphur.

In

$$2CuO + Cu^2S = 4Cu + SO^2$$

1 part of copper as CuO reduces 1 part of copper as Cu^2S, and

causes the elimination of one-fourth its weight of sulphur. Therefore, the sulphur eliminated by the reactions given is:

		Parts.
By reaction of sulphate on sulphide 1.3×1	=	1.3
By reaction of oxide on sulphide $2.1 \times \frac{1}{4}$	=	0.5
Total	=	1.8
Sulphur remaining to form matte $= 7.4 - 1.8$	=	5.6
Sulphur needed to form Cu^2S	=	2.3
Sulphur left to form FeS $= 5.6 - 2.3$	=	3.3
FeS formed $= 3.3 \times 88/32$	=	9.1
Cu^2S formed	=	11.4
Matte formed	=	20.5

$$\text{Per cent of copper} = \frac{9.1}{20.5} = 0.444 = \mathbf{44.4} \text{ per cent.} \qquad (4)$$

In the roasting of ores a large amount of heat is set free, since both the sulphur and the metal are usually oxidized.

Problem 102.

In the ore of Problem 101, taking the data given for its weight before and after roasting, how much heat was generated in its roasting per kilogram of ore treated.

Solution: Starting with 100 parts of original ore it contained 32.6 parts of sulphur and 8.2 of copper. The latter corresponds to 2.05 of sulphur as Cu^2S, which would mean 8.2 of sulphur altogether as chalcopyrite, leaving 24.4 of sulphur present in the ore as iron pyrites.

In 100 parts of roasted ore we have 5.7 parts of copper as Cu^2S, therefore unchanged, 2.1 parts changed to CuO and 1.3 parts changed to $CuSO^4$. These contain sulphur as follows:

	Parts.
Sulphur for 5.7 Cu as Cu^2S	= 1.4
Sulphur for 1.3 Cu as $CuSO^4$	= 0.7
Sulphur for copper compounds	= 2.1
Sulphur for FeS $= 7.4 - 2.1$	= 5.3
FeS $= 5.3 \times 88/32$	= 14.6

Per 90.1 of roasted ore there is present:

Cu as $CuSO^4$	= 1.17
Cu as Cu^2S	= 5.14
Cu as CuO	= 1.89
Fe as FeS = 9.3×.901	= 8.38
Sulphur	= 6.67

We therefore have:

Heat to Decompose Raw Ore.

		Calories.
8.20 Cu as Cu^2S	= 8.20×160	= 1,312
18.85 Fe as sulphide	= 18.85×429	= 8,087
	Sum =	9,399

Heat of Formation of Products.

5.14 Cu as Cu^2S	= 5.14× 160	= 822
1.17 Cu as $CuSO^4$	= 1.17×2,857	= 3,343
1.89 Cu as CuO	= 1.89× 593	= 1,121
25.93 S to SO^2	= 25.93×2,164	= 56,112
9.55 Fe to Fe^3O^4	= 9.55×1,612	= 15,395
9.30 Fe to FeS	= 9.30× 429	= 3,990
	Sum =	80,783

Net heat evolved = 80,783 − 9,399 = 71,384 Calories.
Per 1 kg. of ore = 713 "

In the roasting of copper ore the heat generated by the oxidation of the ore is an important item in the heat required by the furnace. In the above case, for instance, each kilogram of ore developed about one-tenth as much heat as a kilogram of coke, and with proper arrangements for conserving heat, such as thick walls and compact shape of furnace, combined with regeneration of heat from the cooling ore, there is no reason why such an ore should not be made to roast itself. Such a scheme, when practicable, is highly economical in districts where fuel is dear. A long-bedded calciner, with its single hearth and large radiating surface, cannot meet these conditions, but furnaces having superposed hearths and arrangements for discharging cold ore, cooled by the incoming air, such as the Spence and MacDougal furnaces, can work on many ores without using other fuel.

Problem 103.

An improved Spence furnace used at Butte, Mont., calcines 90,000 pounds of concentrates in 24 hours, of the following composition:

	Per Cent.
Copper	9.8
Iron	33.8
Silica	13.3
Sulphur	41.2

Four-fifths of the sulphur is removed, and the roasted ore is practically discharged cold; 1,500 pounds of slack coal, calorific power 6,500, is used per day. The furnace gases contain:

	Per Cent.
CO^2	0.6
SO^2	7.2
H^2O	0.6
N^2	81.3
O^2	10.3
	100.0

and escape into the chimney at 200° C. Ore charged and discharged cold. Furnace has an outside radiating surface of 5,000 square feet.

Required:

(1) The heat balance sheet of the furnace.

(2) The proportion of the heat generated by the roasting of the ore and by the combustion of fuel.

(3) The heat radiated and conducted to the air per square foot of outside surface per minute.

Solution:

(1) Per 100 of ore used the unroasted and roasted ore will contain, respectively:

Copper	9.8	9.8
Iron	33.8	33.8
Silica	13.3	13.3
Sulphur	41.2	8.2

Assuming that the copper remains in the roasted ore, two-thirds as Cu^2S, one-quarter as CuO and one-tenth as $CuSO^4$, while the iron takes the rest of the sulphur to form FeS, the ex-

cess of iron forming half Fe^2O^3 and half Fe^3O^4. We have the composition of the roasted ore as:

Cu^2S	8.2
CuO	3.1
$CuSO^4$	2.0
FeS	17.0
Fe^2O^3	16.4
Fe^3O^4	15.9
SiO^2	13.3
	75.9

The copper and iron existed in the unroasted ore virtually as Cu^2S, FeS and FeS^2, and therefore the 8.2 of Cu^2S and the 17.0 of FeS in the roasted ore can be considered as unchanged. The actual change in the roasting has been the formation of 3.1 CuO and 2.0 $CuSO^4$ from Cu^2S, and the formation of 16.4 Fe^2O^3 and 15.9 Fe^3O^4 from FeS. If we, therefore, subtract from the heat of formation of these amounts of CuO, $CuSO^4$, Fe^2O^3 and Fe^3O^4, and the SO^2 formed, the heat required to resolve the Cu^2S, FeS and FeS^2 into their constituents, we shall get the net heat evolution in the roasting process. The heats of formation involved are:

	Molecular Heat.		
(Cu^2, S)	= 20,300 Calories	= 127 Cal. per kg. of product.	
(Cu, O)	= 37,700 "	= 471 " " "	
(Cu, S, O^4)	= 181,700 "	= 1,136 " " "	
(Fe, S)	= 24,000 "	= 273 " " "	
(Fe^2, O^3)	= 195,600 "	= 1,223 " " "	
(Fe^3, O^4)	= 270,800 "	= 1,167 " " "	
(S, O^2)	= 69,260 "	= 1,082 " " "	

We then have the heat evolved and absorbed as follows:

	Evolved.		*Calories.*
Formation of CuO	3.1× 471	=	1,460
Formation of $CuSO^4$	2.0×1,136	=	2,272
Formation of Fe^2O^3	16.4×1,223	=	20,057
Formation of Fe^3O^4	15.9×1,167	=	18,555
Formation of SO^2	66.0×1,082	=	71,412
	Total	=	113,756

Absorbed.

Decomposition of Cu^2S	4.1 × 127	=	521
Decomposition of FeS	36.1 × 273	=	9,855
	Total	=	10,376

Net heat evolution per 100 of concentrates:

$$113{,}756 - 10{,}376 = 103{,}380 \text{ Calories.}$$

The gases contain 33 pounds of sulphur for every 100 of ore roasted, and the analysis shows there is 0.072 cubic foot of SO^2 in each cubic foot of chimney gas. This weighs $0.072 \times 2.88 = 0.2074$ ounces, and contains just half its weight = 0.1037 ounces = 0.00674 pounds of sulphur. There is therefore produced, per 100 pounds of ore, $33 \div 0.00674 = 4{,}896$ cubic feet of chimney gas.

This contains, from its analysis:

CO^2	29	cub.	ft.
SO^2	353	"	"
H^2O	29	"	"
O^2	504	"	"
N^2	3,981	"	"

and at 200° C. carries heat up the chimney as follows:

	S_m (0 − 200°)		
CO^2	29 × 0.414 =	12	oz. cal. per 1°
SO^2	353 × 0.420 =	148	" "
H^2O	29 × 0.370 =	11	" "
O^2, N^2	4,485 × 0.308 =	1,381	" "
	Sum =	1,552	" "
	=	97 lb. Cal. per 1°.	
	=	19,400 lb. Cal. per 200°.	

The fuel evolves $6{,}500 \times 1{,}500 = 9{,}750{,}000$ pound Calories per day = 10,830 pound Calories per 100 of ore roasted.

(1) BALANCE SHEET PER 100 OF ORE ROASTED.

	Lb. Calories.
Evolved by the fuel	10,830
Evolved by the roasting operation	103,380
Sum	114,210

Loss in chimney gases.....	19,400
Loss by radiation and conduction.....	94,810
Sum	114,210

(2) The proportion of the total heat generated by the ore itself is:

$$\frac{103,380}{114,210} = 0.90 = 90 \text{ per cent.}$$

by the fuel 10 "

The heat lost by radiation and conduction per day is:

	Lb. Calories.
$94,810 \times 900$	= 85,329,000
Per minute	= 59,000

Loss per square foot of surface per minute $= \frac{59,000}{5,000} =$ **11.8** (3)

Problem 104.

The Evans-Klepetko cylindrical roaster used at Butte, Mont., is 19 feet high, 18 feet in diameter, and roasts 80,000 pounds of concentrates daily from 35 per cent sulphur down to 7 per cent (Dr. Peters). The evolution of heat in the roasting operation is sufficient to supply all the heat needed. The stirrer arms are cooled by water circulation, 100 pounds of water being used per minute, and raised in temperature 50° C. Assume the evolution of heat to be 90 per cent as great as in the roasting of ore in Problem 103, and the chimney loss to be correspondingly smaller.

Required:

(1) The heat balance sheet per 100 of ore roasted.

(2) The loss by radiation and conduction per square foot of outside surface of the furnace.

Solution:

(1) *Heat Evolved.*

	Lb. Calories.
90 per cent of 103,380	= 93,040

Heat Distribution.

Heat in chimney gases	= 17,460
Heat in cooling water	= 9,000
Heat lost by radiation and conduction	= 66,580
Sum	= 93,040 (1)

(2) The outside surface consists of the top and bottom and sides. Their area is as follows:

	Sq. Feet.
Sides $18\times3.14\times19$	= 1,074
Bottom $18\times18\times0.78$	= 253
Top	= 253
Total	= 1,580

Loss by radiation and conduction	*Lb. Calories.*
Per 100 of ore	= 66,580
Per day	= 53,264,000
Per minute	= 37,000

Per square foot surface per minute

$$= \frac{37,000}{1,580} = \mathbf{23.4} \qquad (2)$$

It is interesting to note, as comparing this compact cylindrical furnace with the rectangular furnace of Problem 103, that although no fuel is used and cooling water is used, and radiation losses per square foot are greater because of thinner walls, yet the much smaller radiating surface more than counterbalanced these considerations, and permitted the furnace to run more economically.

Thick walls and minimum radiating surface are the requisites for economy of fuel in general, and the *sine qua non* for roasting copper sulphide ores by their own self-generated heat of oxidation.

Pyritic Smelting.

This method of smelting is sometimes called pyrite smelting, because usually practiced on ores rich in pyrite; it is, however, just as applicable to ores rich in pyrrhotite (magnetic pyrites) or chalcopyrite (copper pyrites), and therefore the more general term *pyritic* smelting is really more proper and descriptive of the range of process.

For a full description of pyritic smelting we would refer the reader to the volume " Pyrite Smelting,"[1] a symposium of information contributed by nearly forty metallurgists, and edited by T. A. Rickard, or to Sticht's monograph, " Ueber das Wesen des Pyrit Schmelzverfahrens,"[2] or to Dr. Peters' " Principles of Copper Smelting,"[3] which contains a 125-page chapter upon it.

A brief statement of the principles of the process is as follows: Given an ore containing considerable silica in the free state and a good percentage of pyrite, pyrrhotite or chalcopyrite, it is possible to smelt it down in a shaft furnace to a ferrous silicate slag and a matte by means of cold blast and without using any carbonaceous fuel. Whether fuel is cheap or dear the possibility of dispensing with it when smelting down certain sulphide ores is highly important; yet it is only within a very few years that the principles involved have been well enough understood to make the process a recognized success. As far as the *modus operandi* is concerned, the ore is charged into a shaft furnace, water-jacketed at the boshes and smelting zone, with enough flux to furnish 10 to 20 per cent of CaO or similar alkaline earth base to the slag, and a high pressure of blast is employed, such as would correspond to a high rate of driving in ordinary smelting (up to 3½ pounds pressure per square inch is used). The matte and slag either collect in the well of the furnace or run continuously into an external settler, where they separate as in ordinary smelting. The heat necessary to run the furnace is all supplied by the oxidation of sulphur and iron in the furnace, the former escaping as SO^2 in the gases and the latter as silicate of FeO in the slag. The process may be regarded as a very quick partial roasting of the ore, accompanied by simultaneous formation of melted slag and matte, because of the high temperature generated by the oxidation itself.

There is hardly any process in the whole of metallurgy which invites so strongly to quantitative calculations, such as we are endeavoring to encourage in this treatise; and there are fewer processes which present such a lack of data upon which to base the calculations. Not only are the physical and chemical (thermochemical) data scarce, but the ordinary industrial

1 *Engineering and Mining Journal*, New York, 1905.
2 Wilhelm Knapp, Halle, 1906. Reprinted from " Metallurgie."
3 Hill Publishing Company, New York, 1907.

data, careful details of the running of the furnaces, weights and compositions of charges and products, analyses and temperature of gases, are very largely lacking—most that we have of value are those furnished as recently as 1906 by Robert Sticht, director of the Mount Lyell furnaces in Tasmania, and these apply only to his particular furnaces and operations.

Fundamental Principles.

Taking the simplest case, and supposing FeS^2 and SiO^2 to be charged into a pyritic smelting furnace, we know without a doubt that the FeS^2 becomes approximately FeS at a red heat, and the sulphur thus evolved is driven off at a part of the furnace where there is no free oxygen, so remains in the furnace gases as sulphur vapor. At a temperature of 1400° Sticht has shown experimentally that the FeS becomes something like Fe^7S^5, and it is known that the sulphur in the matte is often less than can correspond to FeS. But the actual temperature of combustion attained at the moment of oxidation in pyritic smelting is higher even than 1,400°, and it is almost certain that as FeS oxidizes, it is heated so intensely that it really goes through two stages, first decomposing to Fe^2S and then oxidizing to FeO:

$$2FeS = Fe^2S + S$$
$$Fe^2S + SiO^2 + 2O^2 = SO^2 + 2FeO.\ SiO^2$$

or, putting it all together:

$$2FeS + SiO^2 + 2O^2 = S + SO^2 + 2FeO.\ SiO^2$$

If we cast up the thermochemistry of this reaction we find a very considerable evolution of heat, easily comparable with the heat of oxidation of carbon, and accounting for the running of the furnace. The thermochemical analysis of the above reaction is:

	Absorbed.	*Calories.*
Decomposition of 2FeS		48,000
	Evolved.	
Formation of 2FeO	= 131,400	
" " SO^2	= 69,260	
" " 2FeO. SiO^2	= 8,900	
		209,560
Excess of heat evolved	=	161,560

The FeS and SiO^2 come into the zone of oxidation already heated to a high temperature by their contact with the rising hot gases. They come to this zone, or focus, heated to at least 1,000°, and perhaps hotter, before they begin themselves to oxidize. The air comes in cool, and we will not credit it with any sensible heat at the moment oxidation begins.

Theoretical Temperature at the Focus.

With these data, and a few reasonable assumptions, we can calculate how hot the focus will become at its hottest point. This calculation is similar to that for the calorific intensity of combustion of a fuel, or the theoretical temperature before the tuyeres of a blast furnace. Making the calculation for the quantities represented by the equation, and assuming

Heat in FeS at 1000° melted	200	Calories
" " SiO^2 at 1000° solid	260	"
" " Slag ($\frac{5}{3}$ weight of FeO): 0.27 (t − 1100) + 300		"
" " Matte ($\frac{1}{3}$ weight of slag): 0.14 (t−1000) + 200		"

we can calculate the theoretical temperature t, to which the slag, matte and gases will be raised by the heat at hand, which latter is the sensible heat in FeS and SiO^2 at, say, 1,000°, plus the heat evolved in the reaction, plus sensible heat in matte at 1000°:

	Calories.
Heat in 2FeS at 1000°: 176 × 200	= 35,200
" " SiO^2 at 1000°: 60 × 260	= 15,600
" of the reaction	= 161,560
" in matte: 80 × 200	= 16,000
Total heat available	= 228,360

Calorific capacity of the products:

$SO^2 = 22.22\ (0.36t + 0.0003t^2)$

$N^2 = 170\ (0.303t + 0.000027t^2)$

Slag $= 240\ [300 + (t-1100)\ 0.27]$

Matte $= 80\ [200 + (t-1000)\ 0.14]$

Sum $= 0.0113t^2 + 135.5t + 5{,}520 = 228{,}360$

Whence t = 1465°C.

The result of our calculation is to show that a temperature sufficient to run the furnace is theoretically obtainable if the weight of slag made, carrying a given weight of FeO, is not too great. Supposing the silica and other slag-forming ingredients are so heavy in comparison to the amount of FeO formed by oxidation that the slag contains only 50 per cent of such FeO, then the weight of slag above would be 288 instead of 240, and the temperature attained only 1,365° instead of 1,465°. This reduction, however, is getting perilously near the temperature necessary to keep the furnace in operation. The formation temperatures of copper blast-furnace slags are 1,100° to 1,200°, and an over-heating of at least 50° is necessary, for practical operation of the furnace. Suppose we put 1,200° as the minimum theoretical temperature which will run the furnace, then the maximum weight of slag can be calculated in the above solution for t, and thence the minimum percentage of FeO.

Let X be the maximum weight of slag, for t a minimum of 1,200°. Then we have:

		Calories.
Heat in SO^2 at 1200°	=	19,248
" " N^2 at 1200°	=	68,422
" " Slag at 1200°	=	330X
" " Matte at 1200°	=	18,240
Whence	$105,940+330X=228,360$	
and	$X=$	371 kg.

Since this maximum weight of slag must contain the $2FeO=144$ kg. of FeO, the minimum percentage of FeO produced by oxidation and going into slag in pure pyritic smelting, must be

$$144\div 371=0.39=\mathbf{39}\text{ per cent.}$$

The margin for working pyritic smelting is ordinarily so small that variations of the temperature of the blast and its humidity must exercise a large influence in the running of the furnace. This coincides with experience as far as the heating of the blast is concerned. At La Lustre Smelter, Santa Maria del Oro, Mr. Koch says that "a warm blast of 200° C. is a *sine qua non* with us; it spelled success; cold blast meant failure." This is, however, an extreme position; many other metallurgists working other ores have run entirely with cold blast, but there

is no doubt that smelting is easier, faster and more regular when using warm blast. No one has yet tried drying the blast, but there can be no doubt that under some circumstances this would contribute greatly to the regularity of running and would increase the theoretical temperature obtainable at the focus or smelting zone.

Use of Auxiliary Coke.

When the amount of slag-forming material in the charges is high, pyritic smelting using cold, ordinary blast may become impossible for lack of sufficient calories to melt the slag and matte. In this case, which often occurs, some coke may be used, the combustion of which to CO^2 at the focus increases materially the heat available and the temperature. If the temperature desired is, let us say, 1,400°, carbon at 1,000° can burn to CO^2, yielding CO^2 and N^2 as products, and give a large surplus of heat to the charge at this temperature.

One kilogram of coke, containing 0.9 kg. of carbon, will form 3.3 kg. of CO^2 (1.67 cubic meters) and 6.35 cubic meters of N^2. The heat generated is 7,290, and adding in the heat in hot carbon at 1,000° (342) we have 7,632 Calories generated. But in the products at 1,400° we have:

	Calories.
CO^2 $1.67\,[0.37+0.00022\ (1400)]\times 1400$	$=1582$
N^2 $6.35\,[0.303+0.000027\ (1400)]\times 1400$	$=3038$
	4620

Surplus, to help the fusion

$$7632-4620=3012 \text{ Calories.}$$

Each kilogram of coke used will therefore melt down, at 1400°,

$$3012 \div 330=9 \text{ kg.}$$

of slag, and thus relieves the situation materially. At Mount Lyell, 0.5, 1.0 and 1.5 per cent of coke (reckoned on the charge) is found necessary, according to the nature of the ore worked. From this we have increasing quantities of coke used up to several per cent, according to the exigencies of the case, and we pass by insensible gradations through partial pyritic smelting to ordinary smelting. As the carbon is increased the sulphides get less and less of the oxygen blown in, and therefore the degree of oxidation of sulphides is lower and the concentra-

tion poorer. The best concentration, using unroasted sulphide ore, is obtained by pure pyritic smelting, if there are enough sulphides present to generate the requisite heat and temperature.

Rate of Smelting.

In all that precedes it has been assumed that the furnace was driven fast enough. Other things being equal, the harder a furnace is blown the more material can be put through it, and the smaller the heat losses by radiation and conduction when expressed per unit of charge treated or of product obtained. It is, therefore, possible to increase the temperature in the focus simply by harder blowing, and thus to decrease the amount of auxiliary coke needed. A similar effect is produced by heightening the urnace shaft, since this increases the regeneration of heat by the charges, they coming to the hot zone more intensely preheated by the ascending gases. The present tendency in pyritic smelting is undoubtedly to increase the rate of driving, heighten the furnace, and thus decrease the auxiliary coke needed and dispense with hot blast, which is somewhat of a complication.

The possibility of smelting in any manner depends on being able to generate the theoretical temperature necessary for running the furnace, and then keeping the rate of smelting per minute per unit area of the smelting zone as high as practicable. This achieves two practical results, viz.: makes the actual temperature of melted-down slag and matte approximate closer to the theoretical temperature of the focus, and gets the largest tonnage through the furnace. As we gradually increase the smelting rate we increase the temperature of the focus, because of decreased radiation losses; but, on the other hand, we tend to decrease the relative amount of oxidation, because of the decreased time that the charge is subjected to oxidation; there must be a certain rate of driving which will attain the maximum of oxidation, *i.e.*, of concentration, and past which increased tonnage is put through at the cost of decreased concentration.

Problem 105.

W. H. Freeland (*Engineering and Mining Journal*, May 2, 1903), at Isabella, Tenn., smelted Ducktown pyrrhotite ore in a water-jacketed Herreshoff furnace, having a cross-sectional

area at the tuyeres of 21.7 square feet. The analyses of the materials used and the products are as follows:

	Charges.			
	Ore.	*Quartz.*	*Slag.*	*Coke.*
Cu	2.744	....	0.73	....
Fe	36.519	1.45	39.20	2.30
S	24.848	0.32	1.75	1.58
SiO^2	18.548	96.79	30.90	8.41
CaO	7.294	0.23	8.51	....
MgO	2.672	....	2.71	....
Zn	2.556	....	2.88	....
Al^2O^3	0.911	0.32	1.90	3.56
Mn	0.770	....	0.85	....
O	....	0.38	11.37	1.00
C	....	....	....	83.86
CO^2	3.138	....	....	....
Loss	....	0.39	....	....

	Products.		
	Matte.	*Flue Dust.*	*Slag.*
Cu	20.00	2.20	0.37
Fe	47.15	30.80	38.84
S	24.00	16.51	1.74
SiO^2	0.44	23.92	32.60
CaO	0.10	4.45	8.24
MgO	....	1.38	3.44
Zn	2.05	2.98	1.54
Al^2O^3	0.82	1.94	1.50
Mn	0.53	0.15	0.80
O	4.91	15.26	10.88

The charges and products per 24 hours and per 1,000 pounds of ore used were

Charges:		
Ore	68.0 tons	1000 lbs.
Quartz	5.4 "	80 "
Slag	9.8 "	145 "
Coke	2.3 "	34 "
Products:		
Matte	8.34 tons	122.65 lbs.
Flue dust	1.75 "	25.71 "
Slag	63.81 "	938.24 "

Blast applied, 4,500 cubic feet displacement per minute, at 17-ounce pressure. Assume temperature of gases 450° C., and that they contain no CO, SO^3 or free O^2 (no analyses are given). Assume matte and slag issuing from the furnace at 1,300° (no temperature given).

Required:

(1) A balance sheet of everything entering and leaving the furnace.

(2) The volume efficiency of the blowing plant.

(3) The heat generated per minute, per square foot of cross-section, in the focus of the furnace.

(4) The theoretical temperature at the focus.

(5) The proportion of the heat generated in the focus by the combustion of carbon and by the oxidation of sulphides.

(6) If hot blast were used what should be its temperature to be able to dispense with the coke charged? Assume that the pressure was increased so as to keep the delivery to the furnace constant per minute.

Per 1000 *of Ore Smelted.*

Charges.		*Matte.*	*Flue Dust.*	*Slag.*	*Gases.*
Ore (1000).					
Cu	27.44	24.53	0.57	2.34	....
Fe	365.19	57.83	7.92	299.44	....
S	248.48	29.44	4.24	16.33	98.47
SiO^2	185.48	0.54	6.15	178.79	....
CaO	72.94	0.12	1.14	71.68	....
MgO	26.72	....	0.35	26.37	....
Zn	25.56	2.51	0.77	22.28	....
Al^2O^3	9.11	1.00	0.50	7.61	....
Mn	7.70	0.64	0.14	6.92	....
CO^2	31.38	....	....	....	31.38
Quartz (80).					
Fe	1.16	....	....	1.16	....
S	0.26	....	....	....	0.26
SiO^2	77.43	....	....	77.43	....
CaO	0.18	....	....	0.18	....
Al^2O^3	0.26	....	....	0.26	....
H^2O	0.71	....	....	....	0.71

Charges.		*Matte.*	*Flue Dust.*	*Slag.*	*Gases.*
Slags (145).					
Cu	1.06	....	....	1.06	....
Fe	56.84	....	....	56.84	....
S	2.54	....	....	....	2.54
SiO^2	44.81	....	....	44.81	....
CaO	12.34	....	....	12.34	....
MgO	3.93	....	....	3.93	....
Zn	4.18	....	....	4.18	....
Al^2O^3	2.76	....	....	2.76	....
Mn	1.23	....	....	1.23	....
O	15.31	6.04	3.93	5.34	....
Coke (34).					
Fe	0.78	....	....	0.78	....
S	0.54	....	....	....	0.54
SiO^2	2.86	....	....	2.86	....
C	28.51	....	....	....	28.51
Al^2O^3	1.21	....	....	1.21	....
O	0.10	....	....	0.10	....
Blast (1,191).					
O^2	274.91	....	....	97.92	176.99
N^2	916.37	....	....	....	916.37
	2450	122.65	25.71	946.16	1355.77

Notes on the Balance Sheet.

The oxygen of the blast goes as SO^2 and CO^2 into the gases and as oxides into the slag. The amount required for the gases is

$$\text{O in } SO^2 = S \times \frac{32}{32} = 100.96$$

$$\text{O in } CO^2 = C \times \frac{32}{12} = 76.03$$

176.99

$$\text{O for Fe} = 330.68 \times \frac{16}{56} = 94.48$$

$$\text{O for Zn} = 26.46 \times \frac{16}{65} = 6.51$$

$$\text{O for Mn} = 8.15 \times \frac{16}{55} = 2.37$$

O in slag	= 103.36
Contributed by charges	= 5.44
Contributed by blast	= 97.92
To burn sulphides and carbon at the focus	= 176.99
Total from blast	= 274.91

(2) The furnace receives 1,191 pounds of blast per 1,000 of ore smelted. This represents at 0° C.:

$$\frac{1191 \times 16}{1.293} = 14{,}738 \text{ cubic feet.}$$

Per 2000 lbs. ore	=	29,475	"	"	
Per 68 tons ore	=	2,004,300	"	"	per day
	=	83,510	"	"	" hour.
	=	1,400	"	"	" minute.
At 50° C.	=	1,477	"	"	" "
Blower displacement	=	4,500	"	"	" "

$$\text{Efficiency of blower} = \frac{1{,}477}{4{,}500} = 0.328 = \mathbf{32.8} \text{ per cent.} \quad (2)$$

[It is high time that practical furnace men should stop giving the mechanical displacement of their blower as the amount of air received by their furnace. They still keep doing that, although the furnace receives only from 85 per cent down to 25 per cent of the given volume. What per cent of the piston displacement the furnace is actually receiving is a highly important datum, but is more often unknown than known to the practical men. It can usually only be found by calculation, as is illustrated in the preceding case. We urge upon practical furnace managers, for their own information and use, to cease being satisfied with *piston displacement*, and to get deeper into the real inwardness of their furnace processes by calculating

the *air actually received* by their furnaces. The two things are enough different to make it always " worth while."]

(3) To calculate the heat generated at the focus we will assume that all the fixed carbon of the coke is there burned to CO^2, and that the rest of the oxygen blown in produces the reaction characteristic of pure pyritic smelting. We have treated per minute

$$\frac{68 \times 2000}{1440} = 94.4 \text{ lbs. of ore.}$$

and the carbon burned per 1000 of ore is 28.51, generating

$$28.51 \times 8100 = 230{,}930 \text{ lb. Calories.}$$

this absorbs

$$28.51 \times 8/3 = 76.03 \text{ lbs. of oxygen.}$$

leaving $274.91 - 76.03 = 198.88$ lbs. of oxygen to oxidize sulphides.

Since, now, $2O^2$ generates by the pyritic smelting reaction 161,560 calories, we have generated per pound of oxygen thus used:

$$161{,}560 \div 64 = 2{,}524 \text{ lb. Calories.}$$

and per 1000 of ore smelted we will have

$$2{,}524 \times 198.88 = 502{,}000 \text{ lb. Calories.}$$

total heat generated

$$502{,}000 + 230{,}930 = 732{,}930 \text{ lb. Calories.}$$

Since this is per 1000 of ore smelted, per minute we have

$$732{,}930 \div 1000 \times 94.4 = 77{,}640 \text{ lb. Calories.}$$

and per square foot of smelting zone area

$$77{,}640 \div 21.7 = \mathbf{3{,}575} \text{ lb. Calories.} \qquad (3)$$

This last figure is extremely useful in determining the relative activity of different furnaces, and in most cases will be a reliable index of the rate at which the furnace is capable of being driven.

(4) Taking as the basis of calculation 1,000 pounds of ore smelted, there is generated at the focus 732,930 pound Calories, there is used 1,190 pounds of blast, and there arrives at the focus all of the charges except the flue dust, CO^2 of ore, H^2O of quartz, and approximately one-quarter of the sulphur. We therefore, have arriving at the focus about

28.51 lbs. of fixed carbon.
526.50 lbs. of sulphides.
621.20 lbs. of inert slag-forming material.

These, assuming them to reach the focus at 1,000°, would bring back into it the following amounts of heat:

Carbon	$28.51 \times 380 =$	10,834 lb.	Calories.
Sulphides, melted	$526.50 \times 200 =$	105,300 "	"
Slag-forming material	$621.20 \times 174 =$	108,089 "	"
		224,223 "	"
Heat generated at the focus	=	732,930 "	"
Total heat available at the focus	=	957,153 "	"

Letting t be the theoretical temperature at the focus, then we have

Heat in Slag	$946\,[300 + (t - 1100)\ 0.27]$
" " Matte	$123\,[200 + (t - 1000)\ 0.14]$
" " S vapor	$76\,[179 + (t - 445)\ 0.11]$
" " SO^2	$35\,[0.36t + 0.0003t^2]$
" " CO^2	$53\,[0.37t + 0.00022t^2]$
" " N^2	$727\,[0.303t + 0.000027t^2]$

[The 76 pounds of sulphur vaporized at the focus is the total sulphur charged, less the 25 pounds assumed as vaporized above the focus, and less the 100.96 pounds oxidized at the focus; the expression is the total heat in 1 pound of sulphur vapor at t, in pound-Calories. The 70 of SO^2 is the weight of sulphur dioxide formed, in pounds, divided by 2.88; the 53 of CO^2 is the weight of CO^2 formed, in pounds, divided by 1.98; the 727 of N^2 is the weight of N^2 divided by 1.26. To be strictly logical the weights of SO^2, CO^2 and N^2 should be first multiplied by 16 to get ounces, and the resulting expression in ounce-

calories divided by 16 to get pound-Calories. We have simply dispensed with these two numerical operations.]

The sum of the calorific capacity of the products at t° is:

$$20{,}098 + 530.5t + 0.0425t^2 = 957{,}153$$

whence $t = \mathbf{1569°}$ (4)

It will be noted that the temperature is much higher than could have been attained by attempting to smelt this mixture without coke. If the coke were omitted from the charge we would be without the 28.51 pounds of fixed carbon and some 5.5 pounds of slag-forming material; the products would be without the CO^2 and the N^2 corresponding to it, and the heat available would be decreased 230,930 pound-Calories from the absence of carbon. If these corrections are made, and it is still assumed that the materials come down into the smelting zone at 1,000°, the theoretically calculated temperature is

$$t = \mathbf{1447°}$$

While this temperature is theoretically sufficient, yet variations in ore quality and temperature and humidity of the air would make running under these conditions much more precarious than with the coke.

(5) This has already been calculated. We found 230,930 pound-Calories to be due to the formation of CO^2 and 502,000 to the oxidation of sulphides, making of the total

31 per cent from oxidation of carbon
69 per cent from oxidation of sulphides. (5)

(6) If coke were dispensed with, the theoretical temperature previously attained, 1,569°, might be reached if the air used were heated. With cold blast we have, under (4), calculated a theoretical temperature of 1,447°. Under these conditions the heat available was altogether 725,266 pound-Calories. But to heat the products, whose heat capacity was

$$20{,}083 + 451.7t + 0.0247t^2$$

to t = 1,569° would require (evaluating) 789,600 pound-Calories, which is 64,334 pound-Calories more than are available. To supply this difference by heating the blast we reckon first

the amount of blast per 1,000 of ore smelted, which will be 862 pounds and its heat capacity:

$$\frac{862}{1.293}(0.303t+0.000027t^2)$$

making this equal to the heat to be supplied, 64,334 lb. Cal. we have

$$202t+0.01805t^2 = 64,334$$

whence

$$t = 313°. \qquad (6)$$

Problem 106.

At Mount Lyell, Tasmania, R. Sticht analyzed the gases at different depths of the shaft in a pyritic smelting furnace, and found them of nearly uniform composition for 6 feet down, leaving out the sulphur vapor, which condensed in taking the samples. At 6 to 7 feet below the top, close to the focus of the furnace, the mean of 5 analyses gave by volume

H^2	0.00
SO^3	0.00
SO^2	7.90
CO^2	3.56
CO	0.00
O^2	0.88
N^2 (difference)	87.66

The CO^2 comes from coke, which it was stated was used to the extent of 1.5 per cent of the charge. The slag contained 53 per cent FeO, 30 per cent SiO^2.

Required:

(1) The percentage of the heat generated in the furnace coming from the oxidation of sulphides and the combustion of carbon.

(2) The heat developed in the furnace per unit of slag formed.

(3) The volume of blast per 1,000 kg. of slag formed.

Solution:

(1) We will assume the reaction of oxidation of sulphides to be

$$Fe^2S + 2O^2 = SO^2 + 2FeO$$

and, in fact, the above analyses are our chief justification for so doing. The air blown in is approximately 20.8 per cent of oxygen by volume, and according to the above equation the oxygen going to form FeO is equal to that going to form SO^2. We have then for the oxygen used

O^2 to form 7.90 SO^2	7.90
O^2 to form —— FeO	7.90
O^2 to form 3.56 CO^2	3.56
O^2 to form 0.88 O^2	0.88
Sum	20.24

O^2 corresponding to N^2 $87.66 \times \frac{20.8}{79.2} = 23.00$

There is thus a small deficit of oxygen, but if the sulphide oxidizing were assumed to be FeS the reaction would be

$$2FeS + 3O^2 = 2SO^2 + 2FeO$$

and the oxygen accounted for from the gases would be only

O^2 to form 7.90 SO^2	7.90
O^2 to form —— FeO	3.95
O^2 to form 3.56 CO^2	3.56
O^2 to form 0.88 O^2	0.88
	16.29

which barely accounts for two-thirds of the oxygen which must have accompanied the nitrogen.

The conclusion must therefore be that the sulphide which is being oxidized is Fe^2S, and not FeS, for otherwise the gas analyses would show impossible conditions.

The oxidation of the sulphides gives for each O^2 thus used $161{,}560 \div 2 = 80{,}780$ Calories, and the oxidation of C to CO^2 97,200. From the above analyses we infer that for 3.56 volumes of oxygen used for CO^2 15.80 volumes were used in oxidizing sulphides. The relative amounts of heat thus generated are therefore:

By carbon $97{,}200 \times 3.56 = 346{,}000 =$ **21.3** per cent.
By sulphides $80{,}780 \times 15.80 = 1{,}276{,}300 =$ **78.7** " " (1)

(2) The production by oxidation of 2FeO (144 kilograms) is accompanied by the production of SO^2 (64 kilograms) and the evolution of 161,560 Calories. The slag being 53 per cent FeO, the slag formed by the reaction is $144 \div 0.53 = 272$ kg. The 64 kg. of SO^2 would be, in volume, 22.22 cubic meters, and would be accompanied in the gases by

$$22.22 \times \frac{3.56}{7.90} = 10 \text{ m}^3 \text{ of } CO^2.$$

which contains $10 \times 0.54 = 5.4$ kg. of C.
whose heat of oxidation to CO^2 is

$5.4 \times 8100 = 43{,}740$ Cal.
but, heat from sulphides $= 161{,}560$ "
total heat available $205{,}300$ "
per kg. of slag $205{,}300 \div 272 =$ **755** Cal. (2)

Per unit weight of charge this heat would be slightly lower.
(3) The oxygen used per 272 kg. of slag is

for SO^2	22.22 m³
" FeO	22.22 "
" CO^2	10.00 "
Total	54.44 "
per kg. of slag	0.20 "
" 1000 kg. of slag	200. "

Volume of air per 1000 kg. of slag made

$200 \div 0.208 =$ **960** cubic meters (3)

SMELTING OF COPPER ORES.

The smelting down to matte is done either in reverberatory furnaces or in shaft furnaces. The charges are usually composed of roasted ore, roasted matte or speiss, mixed with unroasted sulphides, usually concentrates, and with siliceous rock

or limestone as flux. The important reaction during the smelting down is the formation of Cu^2S by the copper present, the formation of other sulphides, mostly FeS, by the larger part of the sulphur left over, and the slagging of the elements which do not enter the matte. If much lead is present metallic lead will separate out, carrying the bulk of the precious metals, but this phenomenon will be considered under the metallurgy of lead. The important subjects for calculation are: the proportions of roasted and unroasted materials to be used, and the proportions of flux to use to make a satisfactory slag.

Some data of importance for calculations on copper smelting have been determined in the author's laboratory by Prof. Walter S. Landis.

A copper matte containing 47.3 copper, 26.2 iron and 23.6 sulphur, was found to have the following thermo-physical characteristics:

Melting point		1,000° C.
Mean specific heat, $0-t$ = Sm	= 0.21104 — 0.0000366t	
Actual specific heat, at t = S	= 0.21104 — 0.0000732t	
Heat content, solid, at 1,000°	=	174 Cal.
Heat content, liquid, at 1,000°	=	204 Cal.
Latent heat of fusion, at 1,000°	=	30 "
Specific heat, at 1,000°	=	0.138

Heat of formation from Cu^2S and FeS not satisfactorily determined.

A copper blast furnace slag containing 35.5 SiO^2, 39.7 FeO, 1.0 MnO, 11.4 CaO, 2.7 MgO, 9.2 Al^2O^3, 0.42 Cu, 0.42 S, was found to have the following characteristics:

Melting point		1,114° C.
Mean specific heat, $0-t$ = Sm	= 0.20185 +0.0000302t	
Actual specific heat, at t = S	= 0.20185 +0.0000604t	
Heat content, solid, at 1,114°	=	262 Cal.
Heat content, liquid, at 1,114°	=	302 "
Latent heat of fusion, at 1,114°	=	40 "
Specific heat, at 1,114°	=	0.269 "

Heat of formation from its constituent oxides = 133 Calories per kg. of slag.

In the case of the slag, its melting point and latent heat of fusion are not nearly as sharply defined as those of the matte, since the matte melts sharply, but the slag goes through a pasty or viscous stage. The values given are the best approximations which could be gotten from the experiments. As regards heat of formation, the constituent oxides were carefully weighed, mixed with a known weight of carbon, and ignited in a Berthelot bomb calorimeter. Several experiments gave satisfactory concordant results, so that the heat of combination of the constituents of this slag may be taken as not far from 133 Calories per kilo of slag. By following this scheme it is possible to measure experimentally the heat of formation of any slag whose analysis is known.

I. Reverberatory Smelting.

In the reverberatory furnace the atmosphere is in no case strongly reducing; it may be varied from weakly reducing to strongly oxidizing, and in the smelting operation usually averages about neutral. The consequence of this is that copper oxides or sulphate in the charge are not deoxidized by carbon, as in the shaft furnace, nor is Fe^2O^3 reduced to FeO by carbon, but the oxygen thus contained in the charge largely goes off with sulphur as SO^2, thus decreasing the amount of sulphur left to form matte, and therefore increasing the percentage of copper in the matte formed. The reactions are mainly:

$$2CuO + 2FeS + 2Fe^2O^3 + 6SiO^2 = SO^2 + Cu^2S + 6FeSiO^3.$$

The slag $FeSiO^3$ is, however, heavy and viscous; it would contain 45 per cent of silica, but runs better and gives a cleaner separation from matte if some lime is added to it. The replacement of 10 per cent of FeO in this silicate by 10 per cent of CaO lowers its melting point from 1,110° C. to 1,010°, and therefore makes a slag that is much easier to keep fluid and of greater fluidity at any given furnace temperature.

Problem 107.

Peters (*Modern Copper Smelting*, p. 446) gives the composition of the average mixture smelted in the reverberatory furnaces at Argo, Col., as

	Per Cent.
SiO^2	33.9
Iron	10.8
$BaSO^4$	15.5
Al^2O^3	5.6
$CaCO^3$	8.5
$MgCO^3$	5.8
ZnO	6.1
Copper	2.0
Sulphur	5.1
Oxygen	6.4
	99.7

The furnace smelts 50 tons of this mixture (charged hot, at 350° C.) in 24 hours, using 13.5 tons of bituminous coal and producing a matte with 40 per cent of copper. Outside dimensions of furnace 20 x 40 x 6 feet. Area of stack, fire-box and hearth 16, 32.5 and 481 square feet, respectively. Temperature of stack gases 1,000° C. Composition of the coal: moisture 1.40 per cent, fixed carbon 54.90, volatile matter 32.90, ash 10.80 per cent; assume 10 per cent more air used than necessary for theoretical combustion. Temperature of slag and matte 1,200°.

Required:

(1) The weight of matte produced, assuming the slag to carry 0.2 per cent of copper (as intermingled matte), and the matte 40 per cent.

(2) The loss of copper in the slag, expressed in per cent of the total copper present.

(3) The percentage of the calorific power of the fuel existing in the stack gases, the slag and the matte.

(4) The heat lost by radiation and conduction in pound-Calories per minute per square foot of furnace surface.

(5) The velocity of the hot gases at the base of the stack.

(6) The horse-power theoretically obtainable by passing the hot gases through a boiler which reduces their temperature to 200° C., and which, together with the steam engine, gives a total thermomechanical efficiency of 7.5 per cent upon the heat furnished to (entering) the boiler.

Solution:

(1) The entire matte formed, that free plus that intermingled with the slag, will be per 100 of ore mixture

$$2.0 \div 0.40 = 5.0 \text{ pounds.}$$

	Pounds.
FeS in this matte = 5.0 − 2.5	= 2.5
Fe in this matte = 2.5 × 56/88	= 1.6
Fe going to slag as FeO = 10.8 − 1.6	= 9.2
FeO in slag = 9.2 × 72/56	= 11.8

Constituents of slag:

SiO^2	= 33.9
FeO	= 11.8
BaO = 15.5 × 153/233	= 10.2
Al^2O^3	= 5.6
CaO = 8.5 × 56/100	= 4.8
MgO = 5.8 × 40/84	= 2.8
ZnO	= 6.1
Weight of slag	= 75.2
Copper in slag as intermingled matte	= 0.15
Intermingled matte lost in slag	= 0.37
Free matte obtained = 5.0 − 0.37	= **4.63** (1)

(2)
$$\frac{0.15}{2.00} = 0.075 = 7.5 \text{ per cent.} \qquad (2)$$

(3) The calorific power of the fuel may be calculated from its proximate analysis by the method of Goutal (*Electrochemical and Metallurgical Industry*, April, 1907, p. 145), as follows:

Pure fuel 1.0000 − 0.1220	=	0.8780
Per cent of this volatile $\frac{0.3290}{0.8780}$	=	37.5 per cent
Calorific power of volatile matter	=	8,650 Cal.
Calorific power (to liquid H^2O):		
Carbon 0.5490 × 8,100	=	4,447 "
Vol. matter 0.3290 × 8,650	=	2,846 "
Sum	=	7,293 "

Water formed = 0.45

Latent heat of vaporization of water

$= 0.45 \times 606.5$ = 273 Cal.

Metallurgical calorific power = 7,020 "

Assuming the volatile matter to be 15 per cent hydrogen, 40 per cent oxygen and 45 per cent carbon, the coal contains:

Hydrogen	0.329×0.15	= 0.049
Volatile carbon	0.329×0.45	= 0.148
Fixed carbon		= 0.549
Total carbon		= 0.697

and the air necessary for combustion and products therefrom are per unit weight of fuel used:

Oxygen for C = $0.697 \times 8/3$	=	1.859 pounds.
Oxygen for H = 0.049×8	=	0.392 "
Sum =	=	2.251 "
Oxygen in coal = 0.329×0.40	=	0.132 "
Oxygen needed from air	=	2.119 "
Air needed = $\frac{2.119 \times 13/3 \times 16}{1.293}$	=	113.7 cu. ft.
Nitrogen therein = 113.7×0.792	=	90.0 "
10 per cent surplus air	=	11.4 "
Volume of CO^2 = $\frac{2.556 \times 16}{1.98}$	=	20.7 "
Volume of H^2O = $\frac{0.455 \times 16}{0.81}$	=	9.0 "

Assuming the tons mentioned are of 2,000 pounds each, the heat generated per 27,000 pounds of fuel used per day is

$$27{,}000 \times 7{,}020 = 189{,}540{,}000 \text{ pound-Calories,}$$

and, therefore, per 100 pounds of ore smelted:

$$189{,}540{,}000 \div 1{,}000 = 189{,}540 \text{ pound-Calories.}$$

The fuel used per 100 pounds of ore being 54 pounds, the products of combustion are 54 times the above calculated volumes, to which must be added

7.4 pounds SO^2 = (7.4×16) ÷2.88 = 41 cubic feet.
6.0 pounds SO^3 = (6.0×16) ÷3.60 = 27 " "
6.7 pounds SO^2 = (6.7×16) ÷1.98 = 54 " "

found later to be driven off the charge. The stack gases and the heat carried out by them are as follows:

CO^2	613×0.59×1,000 =	361.670	ounce-cal.
H^2O	243×0.49×1,000 =	119,070	" "
N^2 / Air	2,738×0.33×1,000 =	903,540	" "
SO^2	41×0.66×1,000 =	27,060	" "
SO^3	27×0.58×1,000 =	15,660	" "
		1,427,000	" "
	=	89,200	pound-Cal.

Proportion of the calorific power of the fuel in the hot gases:

$$\frac{89,200,}{189,540} = 0.47 = \mathbf{47} \text{ per cent.} \qquad (3)$$

To find the heat in the slag tapped, taking Landis's determination of 302 Calories in slag melted at its melting point, 1,114°, and assuming a specific heat in the melted state of 0.27, we have the heat in it per unit weight at 1,200°:

$$302 + (0.27 \times 86) = 325 \text{ Cal.}$$

Heat in total slag:

$$325 \times 75.2 = 24,440 \text{ Cal.}$$

Proportion of calorific power of fuel in hot slag:

$$\frac{24,440}{189,540} = 0.129 = \mathbf{12.9} \text{ per cent.} \qquad (3)$$

To find the heat in the matte, we may take Landis's determination of 204 Calories in matte just melted at 1,000°, and assuming a specific heat of 0.14 we have heat in unit weight at 1,200°:

$$204 + (0.14 \times 200) = 232 \text{ Cal.,}$$

and, therefore, heat in the matte formed:

$$4.65 \times 232 = 1,080 \text{ Cal.}$$

Proportion of calorific power of fuel in melted matte:

$$\frac{1{,}080}{189{,}540} = 0.006 = \mathbf{0.6} \text{ per cent.} \qquad (3)$$

(4) The heat lost by radiation and conduction equals all the heat brought in and generated by combustion and other chemical reactions in the furnace, minus that absorbed by chemical reactions in the furnace, and minus that issuing as sensible heat in the stack gases, slag and matte. The ore mixture being charged hot, at 350° C., and having an assumed specific heat of 0.15, its sensible heat is

	Calories.
$100 \times 0.15 \times 350$	= 5,250
Add heat of combustion of coal	= 189,540
Heat available	= 194,790

The heats of chemical reaction of sulphates and oxides on sulphides are quite complex, and we will show the calculation in detail at the end of the problem. Suffice here to give the end results of the calculation:

	Calories.
Chemical reactions, net *absorption*	16,480
Heat of formation of slag, *evolved*	+ 9,430
Net heat *absorbed* in reactions and combinations	7,050

The heat balance sheet will therefore show:

Available.

	Calories.
Heat in hot charges	5,250
Heat of combustion of coal	189,540
	194,790

Distribution.

In chimney gases	89,200
In liquid slag, tapped out	24,440
In liquid matte, tapped out	1,080
Absorbed in reactions and combinations	7,050
Loss by radiation and conduction	77,020
	194,790

The loss by radiation and conduction per day will be:

		Calories.
	77,020 × 270	= 20,795,000
per minute	20,795,000 ÷ 1,440	= 14,400

The whole outside area of the furnace, including the base, is $2\ (20\times40)+2\ (6\times40)+2\ (6\times20) = 2{,}320$ sq. ft.

Loss in pound-Calories per square foot of surface per minute:

$$14{,}400 \div 2{,}320 = \mathbf{6.2} \text{ pound-Cal.} \qquad (4)$$

(5) The volume of stack gases, at 0° C., has been found to be 3,662 cubic feet per 100 pounds of fuel used, or $3{,}662\times 270 = 988{,}740$ cubic feet per day = 11.4 cubic feet per second. At 1,000° this volume would be

$$11.4\times(1{,}000+273)\div273 = 53.2 \text{ cubic feet.}$$

And since the area of stack cross-section is 16 square feet the velocity of the hot gases entering the stack is

$$53.2 \div 16 = \mathbf{3.3} \text{ feet per second.} \qquad (5)$$

This is a low velocity and shows good design, which will result in better economy of fuel than if high velocity were used.

(6) The gases were found to contain 89,200 pound-Cal. per 100 of ore smelted, or per day:

	89,200 × 1,000	= 89,200,000 pound-Cal.
per hour		= 3,717,000 " "

Since 1 hp. equals 1,400 pound-Cal. per hour, we have:

Horse-power at 100 per cent efficiency:

$$3{,}717{,}000 \div 1{,}400 = 2{,}650$$

Horse-power at 7.5 per cent efficiency:

$$2{,}650\times0.075 = \mathbf{199} \text{ hp.} \qquad (6)$$

In connection with requirement (3) of above problem it will be interesting and instructive to discuss the chemical and especially the thermochemical phenomena accompanying the smelting down of the ore mixture. The discussion will be clearest if we take the actual figures of the problem in question.

Aside from the SiO^2, Al^2O^3, etc., the ore mixture contains:

	Per Cent.
Fe	10.8
Cu	2.0
S	5.1
O	6.4

and these four ingredients are present either as FeS, FeO, Fe^2O^3, $FeSO^4$, Cu^2S, Cu^2O, CuO or $CuSO^4$. With the above quantities of the four elements in question, however, the manner in which they are combined is fixed within rather narrow limits. Each of the four binds each of the others, and it can be found, by some patience and trying out, that the four elements, constituting 24.3 per cent of the ore mixture, must be combined about as follows in order to be present in the quantities given:

	Per Cent
CuO	1.0
$CuSO^4$	3.0
FeS	7.3
$FeSO^4$	8.9
FeO	0.4
Fe^2O^3	3.7

The best proof of this statement is to resolve the weights of these compounds into their components, and to thus prove that they agree with the premises.

On melting this down to 40 per cent matte we produce

Cu^2S	2.5 per cent in matte,
FeS	2.5 per cent in matte,
SO^2	7.4 per cent in gases,
FeO	11.8 per cent to slag.

The heat represented by the formation of the products must be subtracted from the heat of formation of the materials reacting to get the net heat of the reaction. We will multiply the amount of each material by the heat of formation of unit weight from its elements as follows:

		Cal.
CuO	$1.0\times(37{,}700\div 79.6) = 1.0\times 473$	$= 473$
$CuSO^4$	$3.0\times(181{,}700\div 159.6) = 3.0\times 1{,}139$	$= 3{,}417$
FeS	$7.3\times(24{,}000\div 88) = 7.3\times 273$	$= 1{,}993$

$FeSO^4$	$8.9 \times (214,500 \div 152) = 8.9 \times 1,411$	$= 12,558$
FeO	$0.4 \times (65,700 \div 72) = 0.4 \times 913$	$= 365$
Fe^2O^3	$3.7 \times (195,600 \div 160) = 3.7 \times 1,223$	$= 4,525$
		Sum $= 23,331$

Heat of formation of products:

Cu^2S	$2.5 \times (20,300 \div 159) = 2.5 \times 128$	$= 320$
FeS	$2.5 \times (24,000 \div 88) = 2.5 \times 273$	$= 683$
SO^2	$7.4 \times (69,260 \div 64) = 7.4 \times 1,082$	$= 8,007$
FeO	$11.8 \times (65,700 \div 72) = 11.8 \times 913$	$= 10,773$
	Sum	$= 19,782$
	Difference, heat absorbed	$= 3,549$

We have, therefore, a deficit, or heat to be supplied. This deficit is increased by the heat required to decompose $BaSO^4$ into BaO and SO^3, $CaCO^3$ into CaO and CO^2 and $MgCO^3$ into MgO and CO^2; while it is decreased by the heat of combination of Cu^2S and FeS to form matte, and the heat of combination of SiO^2 with BaO, Al^2O^3, CaO, MgO, ZnO and FeO to form slag.

The driving off of SO^3 and CO^2 absorbs

	Calories.
SO^3 from BaO, SO^3 $6.0 \times 1,189$	$= 7,134$
CO^2 from CaO, CO^2 $3.7 \times 1,026$	$= 3,796$
CO^2 from MgO, CO^2 3.0×666	$= 1,998$
Sum	$= 12,928$

The net result of all these reactions, leaving out the formation heat of the slag from its oxide constituents, is

	Lb. Cal.
Absorbed $23,331 + 12,928$	$= 36,259$
Evolved	$19,782$
Deficit	$16,477$

And even if we credit the heat of formation of the slag:

	Lb. Cal.
70.9×133	$= 9,430$
there remains a net deficit of	$7,047$

The reaction of the ore mixture to form matte and slag is therefore an endothermic operation, in spite of the fact that much sulphur goes off as SO^2. The prime reason for this is that the bulk of the sulphur in the roasted ore was present as sulphate and not as sulphide.

Problem 108.

A copper blast furnace has at its disposal materials of the following compositions in percentages:

	Cu.	*Fe.*	*S.*	*SiO².*
Selected raw ore.....	15	20	35	25
Roasted concentrates....	25	35	10	12
Refinery slag.....	50	10	—	25
Limestone.....	CaO — 50			1

It is desired to make a matte with 50 per cent copper and a slag containing 35 per cent SiO^2, 40 per cent FeO and 15 per cent CaO, or with these ingredients in those proportions.

Required:

(1) The proportions of charge.

(2) A balance sheet showing distribution of these materials.

Solution: The foregoing conditions are those which frequently confront the copper smelter. He has at hand raw ore and roasted concentrates, whose relative quantities he can usually vary at will by simply concentrating and roasting more or less material. He has return slags from the refinery furnaces which, however, are not unlimited in quantity, but bear a general relation to the weight of matte made and sent on to the further operations. Finally, the limestone can be varied at will. It will readily be seen that if the charge is fixed at a certain quantity of raw ore to start with, that there are then three variables, the quantities of the other three materials, and to fix these there are practically only two conditions to be fulfilled, the two ratios between three components of the slag. In order to make a solution possible, it is necessary to make an assumption which will practically reduce the number of variables by one, and on looking over the ground it is seen that the most rational assumption which can be made is to assume the refinery slag to bear a given relation to the weight of matte produced. Such an assumption eliminates the weight

of refinery slag as a variable, and leaves us with only two variables and two conditions to fill, which makes a solution possible. Assuming the charges to be based on 100 of roasted ore, we can call the weight of roasted concentrates used X, the weight of refinery slag Y, and the weight of limestone Z, and then figure out the weight of matte produced in terms of X, Y and Z. Assuming then that the refinery slag is, say, 0.25 of the weight of matte, we have $Y = \frac{1}{4}$ (expression for weight of matte), and thus one equation between X, Y and Z. The ingredients of the slag being figured out in terms of X, Y and Z, the assumed relations between FeO, CaO and SiO^2 in the slag give us two more equations between X, Y and Z, and thus all three quantities can be determined.

The provisional balance sheet, based on 100 of ore and X, Y and Z of other ingredients of the charge, will be as follows:

BALANCE SHEET.

Ore. (100).	*Matte.*	*Slag.*
Cu 15	Cu 15	
Fe 20	Fe 7.2+0.14Y	FeO 16.5 – 0.18Y
S 35	S 7.8+0.03X+0.26Y	
SiO^2 25		SiO^2 25.0
R'st'd Conc. (X).		
Cu 0.25X	Cu 0.25X	
Fe 0.35X	Fe 0.12X	FeO 0.30X
S 0.10X	S 0.10X	
SiO^2 0.12X		SiO^2 0.12X
Ref. Slag. (Y).		
Cu 0.50Y	Cu 0.50Y	
Fe 0.10Y	Fe 0.10Y	
SiO^2 0.25Y		SiO^2 0.25Y
Lime-stone. (Z).		
CaO 0.50Z		CaO 0.50Z
SiO^2 0.01Z		SiO^2 0.01Z

Notes on above balance sheet:

Copper in the matte	15	+0.25X+0.50Y
Weight of matte (50 per cent Cu)	30	+0.50X+1.00Y

Weight of S in matte..... $7.8+0.13X+0.26Y$
Weight of Fe in matte..... $7.2+0.12X+0.24Y$

These weights of S and Fe are therefore provided for under the column "matte," taking them from the various materials charged.

The refinery slag being assumed 0.25 of the matte, we have at once

$$Y = 0.25\,(30+0.50X+1.00Y)$$
$$= 7.5+0.13X+0.25Y$$

whence $Y = 10+0.17X$

That is, the refinery slag equals in weight 0.1 the ore plus 0.17 the roasted concentrates. This practically amounts to leaving the roasted concentrates and limestone as the only variables.

The problem can now be solved by summing up the ingredients of the slag as follows:

$$FeO = 16.5-0.18Y+0.30X$$
$$SiO^2 = 25.0+0.25Y+0.12X+0.01Z$$
$$CaO = 0.5Z$$

or substituting

$$Y = 10 +0.17X$$
$$FeO = 14.7+0.27X$$
$$SiO^2 = 27.5+0.16X+0.01Z$$
$$CaO = 0.5Z$$

And since the requirements of the slag are that

$$SiO^2 = \frac{35}{40}\,FeO$$

and

$$CaO = \frac{15}{40}\,FeO$$

we have:

$$27.5+0.16X+0.01Z = \frac{35}{40}\,(14.7+0.27X)$$

$$0.50Z = \frac{15}{40}\,(14.7+0.27X)$$

whence

$$X = 195 \quad Z = 48$$

and, therefore, $Y = 43$

The final balance sheet then becomes

BALANCE SHEET.

Ore.	(100).	*Matte.*	*Slag.*
Cu	15	Cu 15	
Fe	20	Fe 20	
S	35	S 35	
SiO^2	25		SiO^2 25
Rs't'd Conc.	(195).		
Cu	49	Cu 49	
Fe	68	Fe 17	FeO 66
S	20	S 10	
SiO^2	23		SiO^2 23
Ref. Slag.	(43).		
Cu	22	Cu 22	
Fe	4	Fe 4	
SiO^2	11		SiO^2 11
Limestone.	(48).		
CaO	24		CaO 24
SiO^2	1		SiO^2 1
		172	150

Matte.	*Per Cent.*	*Slag.*	*Ratio.*
Cu	86 = 50	SiO^2	60 = 36
Fe	41 = 24	FeO	66 = 40
S	45 = 26	CaO	24 = 14
	172		150 90

Furnace managers are usually afraid of X, Y and Z, and in regular running there is usually little need for an algebraic solution, yet many occasions arise when a judicious use of algebra solves a problem in an exact manner which hardly any amount of guessing or approximating can attain efficiently. In bringing forward this solution we may lay ourselves open to being called pedantic or academic, but the fact is that *the conditions of this problem* were proposed to the writer as a difficult nut to crack by a practical copper smelter, and the algebraic solution furnished was characterized by him as the most satisfactory solution of this class of problems which he had yet seen.

"Bringing Forward" of Copper Matte.

The above term is the old Welsh expression for the further treatment of mattes which gradually eliminates iron and sulphur and finally results in "crude" or "blister" copper, usually 90 to 99 per cent pure. The matte obtained by the first smelting operation varies considerably in richness, between 20 and 50, or even up to 60 per cent, of copper. The reason it is not always made high in copper is that the richer the matte the more copper goes into the slag; one of the expert metallurgist's best accomplishments in copper smelting is to make a rich matte and poor slag. The making of slag of the best composition, and the use of extra large settlers or fore-hearths, helps most to this end. Having then this first "matte" the problem of the metallurgist is to get from it the metallic copper which it contains.

The Welsh Process.

The principle employed is to partially roast the matte and then to smelt it down to a richer matte and a ferruginous slag. The grade of matte formed in this smelting depends entirely upon the amount of roasting to which the matte has been subjected, the more sulphur eliminated by roasting the less can be present to form matte and the richer the matte.

Illustration: A matte containing 21.36 per cent of copper and 22.95 per cent of sulphur is roasted until its sulphur contents is two-thirds eliminated. What grade of matte can be expected on the subsequent smelting.

The sulphur left is $22.95 \div 3 = 7.65$. The 21.36 of copper requires 5.34 of sulphur to form Cu^2S, leaving $7.65-5.34 = 2.31$ of sulphur to form FeS. This forms $2.31 \times 88/32 = 6.35$ FeS. The resulting matte cannot contain more FeS than this; its composition will therefore be approximately:

Copper	21.36	= 64 per cent
Iron	4.04	= 12 "
Sulphur	7.65	= 23 "
	33.05	

In practical work a richer matte than this will be formed in reverberatory furnace smelting and a slightly poorer matte by shaft furnace smelting, because in the former there is some

reaction between the oxides and sulphides of the roasted ore, resulting in an expulsion of SO^2 during smelting, and in the latter, using carbonaceous fuel, the temperature is so high and reducing action so strong that metallic iron is formed and enters the matte, practically acting as if the matte contained some Fe^2S, and thus diluting the matte.

This roasting is a slow operation unless the matte is crushed and roasted fine. Lump matte is very little pervious to gases; it roasts slowly. By breaking a lump in half we, on an average, increase its surface 50 per cent, and therefore the exposed surface available for oxidation increases, for a given weight of material, very quickly as its size is decreased. For autoroasting by its own self-generated heat of oxidation the finer the better, and roasting thus in lump form is impracticable because of the slowness of the operation.

Pyritic smelting of matte is probably altogether out of question as far as pure pyritic smelting without carbonaceous fuel is concerned. Using some coke, however, an oxidizing smelting analogous to partial pyritic smelting is possible, as was proved by Mr. Freeland, at Isabella, Tenn. Such a concentrating pyritic smelting is more feasible with a low-grade matte than with a high grade, because there is more iron and sulphur to oxidize. It will be profitable to calculate closely the details of this matte smelting to rich matte, and to compare it with the details of the smelting of raw ore in the same furnace—the subject of Problem 105, page 463.

Problem 109.

W. H. Freeland at Isabella, Tenn. (see *Engineering and Mining Journal*, May 2, 1903), smelted a low-grade matte without preliminary roasting in a water-jacketed Herreshoff furnace, having a free area at the tuyeres of 21.7 square feet. The analyses of materials used and the products are as follows:

Charges.

		Raw	*Laboratory*			
	Matte.	*Ore.*	*Samplings.*	*Slags.*	*Quartz.*	*Coke.*
Cu.....	20.00	2.79	2.45	0.73	....	....
Fe.....	47.15	43.26	31.07	39.20	1.45	2.30
S.....	24.00	29.18	14.84	1.75	0.32	1.58
SiO^2.....	0.44	10.01	22.66	30.90	96.79	8.41

	Matte.	*Ore.*	*Samplings.*	*Slags.*	*Quartz.*	*Coke.*
CaO	0.10	6.32	5.71	8.51	0.23	....
MgO	....	1.39	2.03	2.71	....	....
Zn	2.05	2.56	2.05	2.88	....	0.00
Al^2O^3	0.82	1.00	1.15	1.90	0.32	3.56
Mn	0.53	0.69	0.75	0.85	....	0.00
O	4.91	....	3.39	11.37	0.38	1.00
C	....	....	13.90	....	....	83.86
CO^2, etc	....	2.80	....	....	....	....
Loss	....	....	....	....	0.39	....

Products.

	Matte.	*Flue Dust.*	*Slag.*
Cu	49.63	2.49	0.60
Fe	25.24	24.79	43.99
S	23.00	8.91	1.19
SiO^2	0.26	31.43	33.72
CaO	....	3.31	2.03
MgO	....	1.18	0.57
Zn	1.53	3.81	2.12
Al^2O^3	....	3.93	2.16
Mn	0.39	0.30	0.50
O	....	3.97	12.86
C	....	15.88	....

The charges and products per 24 hours and per 1,000 of matte used were:

Charges.

Matte	47.5 tons	1,000 lbs.
Raw Ore	8.1 "	170 "
Laboratory samplings	1.6 "	34 "
Slag	7.6 "	160 "
Quartz	15.7 "	330 "
Coke	4.5 "	95 "

Products:

Matte	19.1 tons	401.6 lbs.
Flue dust	0.6 "	12.0 "
Slag	56.1 "	1182.2 "

Blast applied, 4,500 cubic feet displacement, at 17 ounces pressure. Assume temperature of gases 450° C., and that they

contain no CO, SO^3 or free O^2 (no analyses are given). Assume matte and slag issuing from the furnace at 1,300° C. (no temperature is given).

Required:

(1) A balance sheet of everything entering and leaving the furnace.

(2) The volume efficiency of the blowing plant.

(3) The heat generated per minute per square foot of cross-section in the focus of the furnace.

(4) The theoretical temperature at the focus.

(5) The proportion of the heat generated in the focus by the combustion of carbon and by the oxidation of sulphides.

(6) The concentration effected in this smelting.

(1) **Balance Sheet** (per 1000 of *matte smelted*).

Charges.		*Matte.*	*Flue Dust.*	*Slag.*	*Gases.*
Matte (1,000)					
Cu	200.00	199.31	0.30	0.39	....
Fe	471.50	101.36	2.97	367.17	....
S	240.00	92.18	....	....	147.82
SiO^2	4.40	1.04	....	3.36	....
CaO	1.00	....	....	1.00	....
Zn	20.50	6.14	....	14.36	....
Al^2O^3	8.20	....	....	8.20	....
Mn	5.30	1.57	....	3.73	....
O	49.10	....	....	49.10	....
Ore (170)					
Cu	4.74	....	....	4.74	....
Fe	73.54	....	....	73.54	....
S	49.60	....	1.07	14.15	34.38
SiO^2	17.02	....	3.77	13.25	....
CaO	10.74	....	0.40	10.34	....
MgO	2.36	....	0.14	2.22	....
Zn	4.35	....	0.46	3.89	....
Al^2O^3	1.70	....	0.47	1.23	....
Mn	1.17	....	0.04	1.13	....
O	2.40	....	....	2.40	....
CO^2	2.38	....	....	....	2.38

Charges.		*Matte.*	*Flue Dust.*	*Slag.*	*Gases.*
Samplings (34)					
Cu	0.83	....	....	0.83	....
Fe	10.56	....	....	10.56	....
S	5.05	....	....	....	5.05
SiO^2	7.70	....	....	7.70	....
CaO	1.94	....	....	1.94	....
MgO	0.69	....	....	0.69	....
Zn	0.70	....	....	0.70	....
Al^2O^3	0.39	....	....	0.39	....
Mn	0.26	....	....	0.26	....
O	1.15	....	0.48	0.67	....
C	4.73	....	1.91	....	2.82
Slags (160)					
Cu	1.17	....	....	1.17	....
Fe	62.72	....	....	62.72	....
S	2.80	....	....	....	2.80
SiO^2	49.44	....	....	49.44	....
CaO	13.62	....	....	13.62	....
MgO	4.34	....	....	4.34	....
Zn	4.61	....	....	4.61	....
Al^2O^3	3.04	....	....	3.04	....
Mn	1.36	....	....	1.36	....
O	16.90	....	....	16.90	....
Quartz (330)					
Fe	4.78	....	....	4.78	....
S	1.06	....	....	....	1.06
SiO^2	319.41	....	....	319.41	....
CaO	0.76	....	....	0.76	....
Al^2O^3	1.06	....	....	1.06	....
H^2O	2.93	....	....	....	2.93
Coke (95)					
Fe	2.19	....	....	2.19	....
S	1.50	....	....	....	1.50
SiO^2	7.99	....	....	7.99	....
Al^2O^3	3.38	....	....	3.38	....
C	79.67	....	....	....	79.67
H^2O	0.27	....	....	....	0.27

Charges.		*Matte.*	*Flue Dust.*	*Slag.*	*Gases.*
Blast (2,065)					
O^2	476.63	....	....	81.24	395.39
N^2	1588.77	....	....	....	1588.77
	(3854)	401.60	12.01	1176.05	2264.84

Notes on the Balance Sheet.

The sulphur and carbon of the charge passing into the gases are, from the balance sheet, 192.61 and 82.49, respectively. We can assume all the carbon in the gases as CO^2 and all the sulphur as SO^2 except, say, half of that from the ore. This leaves $192.61 - 17.19 = 175.42$ of sulphur to be oxidized at the focus:

Oxygen for sulphur	$= 175.42 \times \frac{32}{32} =$	175.42
Oxygen for carbon	$= 82.49 \times \frac{38}{16} =$	219.97
Total to burn sulphur and carbon at focus		395.39
Oxygen for Fe in slag	$= 499.31 \times \frac{16}{56} =$	142.66
Oxygen for Mn in slag	$= 6.48 \times \frac{16}{55} =$	1.88
Oxygen for Zn in slag	$= 23.56 \times \frac{16}{65} =$	5.77
Total in slag		150.31
Total oxygen in gas and slag	=	545.70
Oxygen furnished by solid charges		69.07
Oxygen furnished by the blast		476.63
Nitrogen furnished by the blast		1588.77

(2) The furnace receives 2,065 pounds of blast per 1,000 of matte concentrated. This represents at 0°:

$$\frac{2065 \times 16}{1.293} = 25{,}550 \text{ cubic feet.}$$

Per 2000 lbs. matte	= 51,100	"	"		
Per 47.5 tons matte	= 2,427,250	"	"	per day.	
	= 101,135	"	"	"	hour.
	= 1,686	"	"	"	minute.
At 50° C.	= 1,958	"	"	"	"
Blower displacement	= 4,500	"	"	"	"

$$\text{Efficiency of blower} = \frac{1{,}958}{4{,}500} = 0.435 = \mathbf{43.5} \text{ per cent.} \qquad (2)$$

(3) To calculate the heat generated at the focus we will assume that all the fixed carbon of the coke is there burned to CO^2, and that the rest of the oxygen blown in produces the reaction characteristic of pure pyritic smelting. There is treated per minute:

$$\frac{47.5 \times 2000}{1440} = 66 \text{ lbs. of matte,}$$

and the carbon burned per 1000 of matte is 82.49 lbs., generating

$$82.49 \times 8100 = 668{,}169 \text{ lb.-Calories,}$$

and absorbing 219.97 lbs. of oxygen. This leaves $476.63 - 219.97 = 256.67$ lbs. of oxygen to oxidize sulphides.

Since by the "pyritic smelting" reaction, $2O^2$ generates 161,560 calories, there is generated per pound of oxygen thus used

$$161{,}560 \div 64 = 2{,}524 \text{ lb.-Calories,}$$

and per 1000 lbs. of matte smelted we have

$$2{,}524 \times 256.67 = 677{,}820 \text{ lb.-Calories,}$$

but heat generated by carbon =	668,170	"	"
Total =	1,345,990	"	"

Since this is per 1000 lbs. of matte smelted, we have, per minute

$$1{,}345{,}990 \div 1{,}000 \times 66 = 88{,}835 \text{ lb.-Calories,}$$

and per square foot of smelting zone area, per minute

$$88{,}835 \div 21.7 = 4{,}094 \text{ lb.-Calories.} \qquad (3)$$

Comparing this with the 732,930 pound-Cal. generated at the focus in smelting 1,000 pounds of ore and the 3,575 pound-Cal.

there generated per square foot per minute, we see that the matte smelting requires more heat per unit of charge, principally because the smelting is done more slowly. Radiation losses are over twice as great per unit of charge treated when concentrating matte than when ore concentrating. This points to the utility of hard driving when smelting matte, as the direction likely to yield greatest economy.

(4) Taking as a basis of calculation 1,000 pounds of matte treated, there is generated at the focus 1,345,900 pound-Cal., there is used 2,065 pounds of blast, and there arrives at the focus all of the charges except the flue dust, CO^2 and H^2O of charges, and approximately one-half of the sulphur contained in the raw ore. We therefore have arriving at the focus approximately:

82.5 lbs. of fixed carbon,
1133.0 lbs. of sulphides.
545.0 lbs. of inert slag-forming material.

These come to the focus preheated by the ascending gases, and assuming them to be preheated to 1,000°, we can find the correction to be used for their sensible heat:

Carbon	$82.5 \times 380 =$	31,350	lb.	Calories.
Sulphides, melted	$1133.0 \times 200 =$	226,000	"	"
Slag-forming material	$545.0 \times 174 =$	94,850	"	"
		352,200	"	"
Heat generated at the Focus		1,345,990	"	"
Total in the hot products, at Focus		1,698,190	"	"

Letting t be the theoretical temperature at the focus, then we have:

Heat in Slag	$1176\,[300+(t-1100)0.27]$
" " Matte	$402\,[200+(t-1000)0.14]$
" " S vapor	$17\,[179+(t-445)0.11]$
" " SO^2	$\frac{351}{2.88}\,[0.36t+0.0003t^2]$
" " CO^2	$\frac{302}{1.96}\,[0.37t+0.00022t^2]$
" " N^2	$\frac{1589}{1.26}\,[0.303t+0.000027t^2]$

The calorific capacity of these products at t° is therefore

$$29{,}858 + 858.7t + 0.1046t^2$$

and making this equal to the heat available at the focus, we have

$$0.1046t^2 + 858.7t + 29{,}858 = 1{,}698{,}190$$

whence $t = \mathbf{1622}°$. (4)

This is 53° higher than we calculated for the same furnace smelting ore, with only one-third as much coke. If the coke were omitted from this charge the theoretical temperature would be:

$$t = \mathbf{1388}°.$$

Such a theoretical temperature at the focus would not suffice to form slag, supply radiation and conduction losses, and see the matte and slag safely out of the furnace, except with very hard driving and very fast running in a large furnace.

(5) The heat generated by oxidation at the focus has already been calculated. The proportion to credit to carbon is

$$\frac{668{,}170}{1{,}345{,}990} = 0.496 = \mathbf{49.6} \text{ per cent.}$$

and to oxidation of sulphides **50.4** " (5)

In the ore smelting these figures were found to be 31 and 69 per cents, respectively.

(6) The ratio of concentration is usually found by comparing the per cent of copper in the material treated with that in the material produced. This would give in this case:

$$\frac{49.64}{20.00} = \mathbf{2.48} \quad (6)$$

A more reasonable factor, however, is the ratio of weight of fresh copper-bearing materials treated to weight of copper-bearing materials produced which must be further treated. This would be in this case:

$$\frac{1204}{414} = 2.9$$

whereas in the ore smelting it was

$$\frac{1080}{148} = 7.3$$

"Blister-Roasting" or "Roasting-Smelting."

When a matte has been concentrated to somewhere between 70 and 80 per cent of copper it is called "white metal," and is in shape for reduction to metallic copper:

	Cu^2S.	FeS.
With 70 per cent copper, matte contains...	87.5	12.5
With 80 per cent copper, matte contains...	100.0	0.0

The problem being to get metallic copper, the operation is entirely one of oxidation; first, slow melting down of the lumps of matte in a highly oxidizing atmosphere on the hearth of a reverberatory furnace; second, continued oxidation until all the sulphur is removed and the bath remains as metallic copper, saturated with Cu^2O and Cu^2S.

During the melting down the matte is oxidized superficially to such an extent that when fusion is finally complete the copper oxides have reacted upon the iron sulphides sufficiently to eliminate all the iron from the matte. The reactions and phenomena of this period are exactly those of the matte concentration processes.

After the melting down sulphur continues to be oxidized with formation of copper oxide, and then this latter reacts with more of the sulphide to set free metallic copper.

(a) $2Cu^2S + 3O^2 = 2Cu^2O + 2SO^2.$

(b) $Cu^2S + 2Cu^2O = 6Cu + SO^2.$

(c) $Cu^2S + O^2 = Cu + SO^2.$

Reactions (a) and (b) are probably consecutive, but assuming them simultaneous we have equation (c).

Thermochemically, equation (a) analyzes as follows:

$2(Cu^2, S)$	= 2(20,300)	= 40,600 Calories	*absorbed.*
$2(Cu^2, O)$	= 2(43,800)	= 87,600 "	*evolved.*
$2(S, O^2)$	= 2(69,260)	= 138,520 "	"
	Algebraic sum	= 185,520 "	"
Per kilo. of Cu^2S		= 580 "	"

Similarly, equation (b):

(Cu^2, S)		= 20,300 Calories	*absorbed.*
$2(Cu^2, O)$	= 2(43,800)	= 87,600 "	"
(S, O^2)		= 69,260 "	*evolved.*
	Algebraic sum	= 38,640 Calories	*absorbed.*
Per kilo. of Cu^2S		= 243 "	"

Equation (c) gives:

(Cu^2, S)		= 20,300 Calories	*absorbed.*
(S, O^2)		= 69,260 "	*evolved.*
	Algebraic sum	= 48,960 "	"
Per kilo. of Cu^2S		= 308 "	"
Per kilo. of copper liberated		= 385 "	"

The net result of these figures is to show that the first reaction evolves a large amount of heat, that the second absorbs considerable, but that the two together constitute a highly exothermic reaction. When we reflect that a kilogram of melted Cu^2S only carries some 250 Calories, and a kilogram of melted copper not over 200 at any furnace temperature, the excess of heat above calculated shows up very strikingly.

In a reverberatory furnace the rate of oxidation is so slow that but minor advantage is taken of the heat of oxidation of the Cu^2S.

Illustration: In a reverberatory furnace, 8 tons of " white metal " is smelted to blister copper in 48 hours, using 5 tons of coal. About what proportion does the heat of oxidation of the charge bear to the heat of combustion of the coal?

Assuming the tons to be 1,000 kilos., the white metal to be

nearly pure Cu^2S, and the calorific power of the coal 6,000, we have:

Heat of oxidation of the bath	8000×308	= 2,464,000	Calories.
" of combustion of coal	5000×6000	= 30,000,000	"
" requirement for 48 hours		32,464,000	"
" requirement per hour		676,333	"

Proportion of heat requirement furnished by oxidation of bath:

$$\frac{2,464,000}{34,920,000} = 0.759 = \mathbf{7.6} \text{ per cent.}$$

The above figures teach us, however, that when the charge is once melted, if the oxidation of the bath could be performed quickly enough it alone would keep the furnace up to heat. For example, the furnace requires an average of 727,500 Cal. per hour to keep it up to heat. The heat of oxidation would therefore supply this for

$$\frac{2,464,000}{727,500} = 3\tfrac{1}{2} \text{ hours,}$$

which means that if the bath, when melted, could be oxidized in that time all exterior firing would be unnecessary after the charge had been once melted. Some companies force air onto the surface of the bath, and one company blows compressed air through wrought iron pipes into the bath, producing the required oxidation in one-fifth the time usually required, and saving greatly in coal.

Bessemerizing Copper Matte.

John Hollaway, in 1878, patented the process of oxidizing matte to metallic copper in an apparatus similar to the Bessemer steel converter; in 1880, Manhès, in France, was successful in accomplishing this result, and in 1884 ran the first commercial plant at the Parrot works in Butte. While the principles are similar the details are very different from the blowing of pig iron to steel.

In oxidizing pig iron the carbon silicon, manganese, etc., which are to be oxidized out rarely exceed 10 per cent, while

the iron itself is oxidizable, and some 3 to 20 per cent may be lost. In oxidizing matte some 40 to 70 per cent of the whole charge is to be oxidized, a very voluminous slag results, and the operation lasts five to fifteen times as long. Towards the end of a " steel " blow, the pure iron formed is itself oxidizable, and is not chilled but really heated by the passing of the blast through it; in a " matte " blow the pure copper separating at the end is not oxidizable under the prevailing conditions, and therefore is only chilled by the blast if the latter strikes it. On the latter account, tuyeres in the bottom are impracticable when Bessemerizing matte, since they become filled with chilled copper; it is imperative to use lateral tuyeres which, by the swinging of the converter, are kept always below the surface of the matte but above the pool of copper as it separates out and sinks to the bottom.

The two best treatises for details of bessemerizing copper matte are *Jannettaz's "Les Convertisseurs pour le Cuivre" and Dr. F. Mayr's " Das Bessemern von Kupfersteinen; " very satisfactory information can be found in Dr. Peters' " Modern Copper Smelting " and " Principles of Copper Smelting," in Hixon's " Notes on Lead and Copper Smelting and Copper Converting," and in Schnabel's " Handbook of Metallurgy," last edition, Vol. I.

Assume that a converter is just emptied, is at a bright red heat (1,100°), and that a charge of melted matte at, say, 1,100° (setting point 1,000°), is poured into it. The lining is some 60 cm. thick, the outside shell of the converter is at about 200° C., and the surface is losing heat at a nearly steady rate of, say, 50 Cal. per square meter of outside surface per minute (10 pound-Cal. per square foot). A converter of 25 square meters outside surface would thus lose 1,250 Cal. per minute if standing still. If it had 3,000 kg. of liquid matte in it, with a specific heat of 0.14, the latter would give out $3,000 \times 0.14 = 420$ Calories for every degree which it cooled, and would therefore cool off about $1,250 \div 420 = 3°$ per minute. If poured in 100° above its setting point it might be some 30 minutes in cooling to its setting point and 70 minutes in setting, assuming no radiation losses through the throat, *i.e.*, that the throat were tightly covered.

* Mem. de la Soc. Ing. Civile, 1902, (I), 268–319.

Under such conditions, if blast is turned on, the reaction is

$$2FeS + 3O^2 + 2SiO^2 \text{ (lining)} = 2(FeO, SiO^2) + 2SO^2$$

and the heat evolved is

Decomposition of	$2FeS$	$= 2(24,000)$	$= -48,000$ Calories.
Formation of	$2FeO$	$= 2(65,700)$	$= +131,400$ "
Union of $2FeO$ with	$2SiO^2$	$= 2(8,900)$	$= +17,800$ "
Formation of	$2SO^2$	$= 2(69,260)$	$= +138,520$ "
		Total	$= +239,720$ "

Heat evolution per 1 kg. FeS	=	1,362 Calories.
Heat evolution per 1 kg. O^2	=	2,497 "

Theoretical Temperature Rise.

Supposing we oxidize an amount of FeS equal to 1 per cent of the weight of matte. Let us calculate the theoretical rise in temperature of the contents of the converter.

The oxygen required is $3O^2$ to $2FeS$, or per kilo. of FeS.

Oxygen required $= 96 \div 176$	$= 0.545$ kg.
N^2 accompanying	$= 1.818$ "
Air required	$= 2.363$ "
Volume $= 2.363 \div 1.293$	$= 1.827$ m³.

In being raised from say 50° C. to 1100°, the assumed temperature of the matte, the air will absorb

$$1.827[0.303 + 0.000027(1150)] \times 1050 = 641 \text{ Calories.}$$

This leaves available, for raising the temperature of the products of the reaction:

$$1,362 - 641 = 721 \text{ Calories.}$$

The immediate products are:

99. kg. of unoxidized matte.
1.50 " " liquid slag.
0.73 " " SO^2 gas.
1.82 " " N^2 gas.

The heat capacities of these, at 1100°, are as follows, per 1° C.:

Matte	99×0.14	= 13.86	Calories.
Slag	1.50×0.27	= 0.41	"
SO^2	$0.73 \div 2.88 \times 1.02$	= 0.25	"
N^2	$1.818 \div 1.26 \times 0.36$	= 0.52	"
		Sum = 15.04	"

Theoretical temperature rise

$$721 \div 15.04 = 47.9° \text{ C.}$$

The above rise represents the *rate* at which the temperature tends to rise at the beginning of the blow. Supposing this amount of FeS (1 per cent) is oxidized in 1 minute, the temperature at the end of 1 minute would rise 47.9° less the cooling off in 1 minute, which latter might be from 2° to 10°, according to the size of the converter and its charge, thickness of lining, etc. For practical purposes the cooling-off rate may be assumed as nearly constant, but the heating-up rate is quite variable. As the FeS disappears the amount of slag increases, while that of the matte decreases; but since 1.50 kilos. of slag with a calorific capacity of 0.41 Cal. per degree takes the place of 1 kilo. of matte with a calorific capacity of 0.14 Cal. per 1°, the heat capacity of the products is increasing 0.27 Cal. for each 1 per cent. of FeS oxidized, while the available heat for raising temperature is slightly decreasing, because of the higher temperature of the bath and therefore the greater chilling effect of the air. Assuming that the bath cools 5° during the time that 1 per cent of FeS is being oxidized out, we can calculate the following table:

FeS Oxidized.	*Temp. at Start.*	*Heat Absorbed by Air.*	*Net Heat Available.*	*Calorific Capacity of Products.*	*Temp. Rise.*
0 to 1%	1100°	641	715	15.04	42.9°
1 " 2%	1142.5°	670	686	15.31	40°
2 " 3%	1182°	694	662	15.58	37°
3 " 4%	1219°	722	634	15.85	35°
4 " 5%	1254°	742	614	16.12	33°
5 " 6%	1287°	768	588	16.39	31°

FeS Oxidized.	Temp. at Start.	Heat Absorbed by Air.	Net Heat Available.	Calorific Capacity of Products.	Temp. Rise.
6 " 7%	1318°	789	567	16.66	29°
7 " 8%	1347°	809	547	16.93	27°
8 " 9%	1374°	823	533	17.20	26°
9 " 10%	1405°	847	509	17.47	24°
At 10%	1429°	...	...	.....	...

There is no object in extending above table, because it is constructed on the particular assumption that radiation losses would amount to 5° during the burning out of 1 per cent of FeS. This quantity would evidently vary with the size of the converter, the amount of matte being treated and the speed of blowing, because as the contents become hotter their rate of cooling would be increased. The object of the above table, so far as it went, was to show that 47.5° was the theoretical rise for the first 1 per cent, but that the theoretical rises for succeeding per cents would be less and less; in such manner, instead of rising $(47.9 - 5) \times 10 = 429°$ for an oxidation of 10 per cent of FeS the actual rise figures out only 329°.

One of the most necessary data which is badly needed for these converters, and in fact for Bessemer converters in general, is the heat loss by radiation and conduction, in other words, how much heat would be lost by the charge if simply standing still, how much would the temperature of a given charge fall per minute if standing still. This could be easily obtained by running in a charge of pretty hot matte, and following its temperatue curve as it cools, without any necessity of letting it freeze, but merely starting up the blast when the rate of cooling has been satisfactorily determined. If these determinations were coupled with details as to the temperature of the outside air, its velocity of impingement against the converter, the temperature of the outside shell, the area of radiating surface and the thickness of the lining, we would soon get data with which to render entirely definite and exact the whole thermal investigation of a " Bessemerizing " operation. This should be supplemented by analyses of the gases during the blow and the temperature curve of the contents as the blow

progresses. Scientific metallurgists must, at present, simply assume many of these data, because of lack of them. We are looking to the metallurgical directors of copper plants for some of this badly-needed technical data.

Problem 110.

W. Randolph Van Liew (*Trans. Am. Inst. Mining Eng.*, 1904, p. 418) gives the following analyses of a charge of matte blown to blister copper in a Bessemer converter:

	Cu.	*Fe.*	*S.*	*Zn.*
Matte	49.72	23.31	21.28	1.19
10 minutes	50.20	23.15	20.95	1.20
20 "	56.88	17.85	19.74	0.84
30 "	64.60	10.50	18.83	0.70
40 " (last slag skimmed)	76.37	2.40	16.30	0.45
70 " (blister copper)	99.120	0.038	0.159	0.09

	As.	*Sb.*	*Ag.*	*Au.*
Matte	0.11	0.14	0.152	0.00055
10 minutes	0.09	0.12	0.147	0.00048
20 "	0.08	0.10	0.176	0.00069
30 "	0.08	0.13	0.191	0.00083
40 " (last slag skimmed)	0.08	0.13	0.240	0.00110
70 " (blister copper)	0.0012	0.006	0.312	0.00111

The percentage composition does not exhibit clearly the relative time and amount of the elimination of impurities, because of the varying weight of the bath.

Required:

(1) Assuming 1,000 kilograms of matte to be treated, find the weight of the matte at each period of the blow.

(2) The loss of each constituent of the bath during each period.

(3) The heat evolution during each period.

(4) The loss of heat per minute due to radiation and conduction, assuming that the heat starts with matte at 1,100° and ends with blister copper at 1,200°, and that 1 per cent of copper (reckoned on the matte) is oxidized during the last period.

(1) The first question is to find some constituent of the matte whose weight does not vary during the blow, to serve as a basis for the calculations. If the analyses be taken as reliable in all details (we can make no other assumption) we see that there is very little loss of anything in the first 10 minutes, evidently because of the low temperature of the matte. Afterwards, iron falls off rapidly, also sulphur and zinc, while silver and gold increase in percentage, because of the falling off in weight of the bath as a whole. The slag up to the last skimming, contains usually but very little copper; in the last period we are told to assume a loss of 10 kilos of copper by oxidation. The most rational basis for calculating the weight of the bath is to assume the copper contents constant for the first 40 minutes.

Copper in 1000 kg. of matte at starting			=	497.2 kg.
Weight of matte at starting				1000.0 "
" " "	10 minutes	= 497.2 ÷ 0.5020	=	990.4 "
" " "	20 "	= 497.2 ÷ 0.5688	=	874.1 "
" " "	30 "	= 497.2 ÷ 0.6460	=	769.7 "
" " "	40 "	= 497.2 ÷ 0.7637	=	651.0 kg.
" " metal	70 "	= 487.2 ÷ 0.9912	=	491.5 "

(1)

From the analyses given, and calling the shortage of percentage in the analyses oxygen, we have the following table of weights and eliminations: (2)

Per 1000 *kg. of Original Matte.*

	Cu.	*Fe.*	*S.*	*O.*
Start.....	497.2	233.1	212.8	41.0
Eliminated.....	**0.0**	**3.8**	**5.3**	**0.1**
End 10'.....	497.2	229.3	207.5	40.9
Eliminated.....	**0.0**	**73.3**	**35.0**	**2.9**
End 20'.....	497.2	156.0	172.5	38.0
Eliminated.....	**0.0**	**75.2**	**27.6**	**—0.3**
End 30'.....	497.2	80.8	144.9	38.3
Eliminated.....	**0.0**	**65.2**	**38.8**	**12.0**
End 40'.....	497.2	15.6	106.1	26.3
Eliminated.....	**10.0**	**15.4**	**105.3**	**24.9**
End 70'.....	487.2	0.2	0.8	1.4

Zn.	*As.*	*Sb.*	*Ag.*	*Au.*	
11.9	1.1	1.4	1.52	0.0055	=1000.0
0.0	**0.2**	**0.2**	**0.06**	**0.0007**	**= 9.6**
11.9	0.9	1.2	1.46	0.0048	= 990.4
4.6	**0.2**	**0.3**	**—0.08**	**—0.0012**	**= 116.3**
7.3	0.7	0.9	1.54	0.0060	= 874.1
1.9	**0.1**	**—0.1**	**0.07**	**—0.0004**	**= 104.4**
5.4	0.6	1.0	1.47	0.0064	= 769.7
2.5	**0.1**	**0.2**	**—0.09**	**—0.0008**	**= 118.7**
2.9	0.5	0.8	1.56	0.0072	= 651.0
2.5	**0.5**	**0.8**	**0.03**	**0.0017**	**= 159.5**
0.4	0.0	0.0	1.53	0.0055	= 491.5

Our table is not absolutely accurate, as can be seen from an apparent gain in both silver and gold in the periods $10' - 20'$ and $30' - 40'$. This is caused by a loss of copper during those periods, but the amounts of gold and silver are too small to serve as a base for revising the table. If we were to assume the gold as constant it would make a smaller weight of bath at the ends of those periods, but the figures are not reliable enough to make this correction worth while.

The very small total loss in the first 10 minutes and the loss of time thus occasioned, could in all probability be obviated by putting the matte hotter into the converter at the start.

A graphic representation of the course of a blow is usually made by plotting the *percentages* of each element in the bath at given periods. *This plan is largely misleading*; the diagram should be made by plotting the calculated *weights* of each element present at the given period, such as are found in the above table.

(3) The heat evolution is to be found by taking the weights of each element oxidized out, calculating the heat of its oxidation and formation of slag, and subtracting the heat necessary to break up the equivalent amount of its sulphide. The heat necessary to separate the sulphides from each other is unknown.

Period I.—Start to 10′.

Heat of oxidation:		*Cal.*	*Cal.*
Fe to $FeO.SiO^2$	3.8×1332	= 5,062	
S " SO^2	5.3×2164	= 11,469	

			Cal.	*Cal.*
As " As^2O^3	0.2×1043	=	209	
Sb " Sb^2O^3	0.2×695	=	139	
				16,879

Decomposition of sulphides:

Fe from FeS	3.8×429	=	1630	
As " As^2S^3	0.2×2000 (?)	=	400	
Sb " Sb^2S^3	0.2×1433	=	287	
				2,317
Net heat evolution				14,562

The other periods are similarly calculated, and yield the following results:

	Start–10′	10′–20′	20′–30′	30′–40′	40′–70′	⅓ last.
Heat of oxidation.....	16,879	179,797	162,476	174,316	257,046	85,682
Decomp. of sulphides.....	2,317	35,321	33,719	30,113	10,410	3,470
Net heat evolution.....	14,562	144,476	128,757	144,203	246,636	82,212

The last column is added for comparison, being the heat evolution per average 10′ in the last period. (3)

(4) The loss of heat by radiation and conduction can be found, as a whole, by assuming the converter body to contain the same heat at finishing as at starting, which is a likely assumption, since the lining loses somewhat in weight but ends up at a higher temperature. Then we know how much heat was in the original matte at 1,100°, how much was generated, how much is in the slag and copper, and can calculate approximately how much is carried out in the gases. These enable us to find, by difference, the loss by radiation and conduction which can then be averaged up per minute.

	Calories.
Heat in 1000 of matte at 1100°	= 214,000
Net heat generated in the blow	= 678,635
Total available	= 892,635

Heat in 491.5 Copper, at 1200°	=	85,995
" " 424.0 SO^2, " 1000°	=	97,020
" " 947. N^2, " 1000°	=	248,160
" " 550. Slag, " 1250°	=	187,000
Heat accounted for		618,175
Loss by radiation and conduction	=	274,460
Loss per minute, per 1000 kg. matte	=	**3,920** (4)

It is thought that the principles explained and the methods of calculation illustrated will suffice to show to copper metallurgists how important information is obtainable by applying the principles of thermochemistry to copper smelting, and to indicate the lines along which experiment and results of measurement and observation are greatly to be desired.

THE ELECTROMETALLURGY OF COPPER.

The electric current is used in metallurgy either for its electrolytic effect or for its electrothermal action. In the former the property of the current utilized is its ability when passing in one direction through an electrolyte, of causing at the cathode a *reducing* action, such as the separation of metal from the electrolyte or the reducing of a ferric salt to a ferrous salt, and at the anode a *perducing* effect, the direct opposite chemically of reducing, such as the taking of a metal into the electrolyte or the perducing of a ferrous or cuprous salt to a ferric or cupric condition. In such a process heat is inevitably generated to some extent by the passage of the current through the ohmic resistance offered by the electrolyte. The extent to which heat is thus generated, coincident with the electrolytic action of the current, is of no significance whatever upon the nature of the process, which remains essentially *electrolytic* as long as the current is used for and performs its electrolytic decomposing function. However, when the heat thus coincidently and inevitably generated in the operation of a process essentially electrolytic, is sufficient to keep melted an electrolyte which is not liquid at ordinary temperatures, the apparatus as a whole may not improperly be regarded as a furnace, and is very properly classed as an *electrolytic furnace.*

Electrothermal processes are those characterized by the absence of electrolysis, as shown by the arrangement and working of the apparatus, use of alternating current, etc., and in which the current is used solely for its heating effects. Such processes are carried on in electric furnaces, and are essentially processes in which chemical reactions or physical changes are brought about in the charge solely by the action of the temperature maintained by the assistance of the electric current. Metallurgically, the furnaces used are resistance furnaces, arc furnaces and combinations of the two. In resistance furnaces the heat operating the furnace is produced through the agency of the resistance of the substance or charge itself, or of a solid, liquid or granular resistor, intermingled with, in contact with, or placed in the neighborhood of the material to be heated. In arc furnaces the current jumps a gap between two poles, and generates locally the very high temperature of the arc, which is utilized by feeding the material to be treated into it or by bringing in close proximity to it. In the combined arc-resistance furnace, the material being treated forms one or both poles of the arc, and is therefore heated by the arc itself as well as by the passage of the current through its own substance.

In electrolytic processes the output of material, or commercial efficiency of the process, is essentially dependent upon the amperage of the current, since electrolytic effects are proportional to the amperes passing through the electrolyte. In electrothermal processes the commercial efficiency of output will vary with the total energy dropped by the current in the furnace, *i. e.*, will be proportional to the watts of current used up, not to its amperage or voltage, but to the product of these. Direct currents only are employed in electrolytic processes; direct or alternating may be used in electrothermal processes, but alternating are preferred, because of the complete absence of one-sided electrolytic effects when they are used.

Assuming familiarity with the ordinary non-electric metallurgy of copper, we may divide the electrometallurgy of copper into the following classes:

I. Electrolytic processes—

1. Direct treatment of ores.
2. Treatment of matte.

3. Extraction from solutions.
4. Refining of impure copper.

II. Electrothermal processes—

1. Direct smelting of ores.
2. Melting and casting of copper.

I.

Electrolytic Processes.

Copper has an atomic weight of 63.6. It occurs chemically as cuprous compounds, formulæ CuA^{I}, or cupric compounds, formulæ CuA^{II}, where A^{I} is a univalent or monad acid radicle and A^{II} a bivalent or dyad acid radicle. As a monad atom, copper has a chemical equivalent of 63.6, as a dyad element 31.8. The amounts of copper dissolved into or deposited from a cupric or cuprous salt are proportional to the chemical equivalent of copper in these two states and to the amperes flowing. Assuming that 1 ampere liberates electrolytically 0.00001036 grams of hydrogen per second, we will have as the amount of copper concerned in the passage of 1 ampere through one tank:

	Cuprous Compounds.	*Cupric Compounds.*
1 Ampere, per second..	0.0006589 grams	0.0003295 grams
per minute ..	0.03953 "	0.01977 "
per hour.....	2.372 "	1.186 "
per day.....56.93	"	28.46 "
per year.....20.78	kilograms.	10.39 kilograms

A useful datum to remember, if one is used to working in English measures, is that one ampere deposits practically one ounce avoirdupois (28.35 grams) of copper per day in each cell using cupric compounds, and 2 ounces for cuprous compounds, or, respectively, one-sixteenth and one-eighth of a pound per day. These figures, are of course, the theoretical figures for an ampere efficiency of 100 per cent.

I. 1.—Treatment of Ores by Electrolysis.

There are no native ores of copper susceptible of being melted and electrolyzed—in the manner for instance, that sodium nitrate (Chili saltpeter) can be melted and electrolyzed for the production of sodium. The most abundant ore of copper, its

sulphide, occurs mostly mixed with several times its weight of foreign material, and even if picked out pure and melted it redissolves copper at the cathode so actively that no electrolysis is possible. Faraday showed that melted cupric oxide is decomposed by the current; and if the oxides of copper were found anywhere in sufficient purity and quantity they could be melted and decomposed electrolytically, but hardly in any case as cheaply as they can be reduced by carbonaceous material.

Cupric chloride is found in nature as atacamite, with the formula $CuCl^2$. $3Cu^2O$. $2H^2O$, in a comparatively pure condition, but in small quantity, in Chili. Such material will dissolve in considerably quantity in melted salt (NaCl), and can then be electrolyzed. The dissolved copper salt is first reduced by the current, with evolution of chlorine, to CuCl, and then this decomposed. The quantity of this material is at present insignificant, but there is a possibility of an electrolytic process along this line.

Cuprous chloride does not occur in nature, but can be readily made from other copper-bearing material. Chlorine gas, for instance, converts the common copper sulphide, Cu^2S, into CuCl (Ashcroft's process). When melted, cuprous chloride conducts the current very well, copper separating out as fine leaves. The melt cannot be heated to the melting point of copper and the copper obtained liquid, because it vaporizes too easily. It is a good conductor, its resistivity at 50° above its melting point being only 6 ohms (per centimeter cube).

Problem 111.

In electrolyzing a bath of melted cuprous chloride, using an unattackable anode, the electrodes are 4 centimeters apart, and a current density of 0.5 amperes per square centimeter is used.

Required:

(1) The voltage required for running the bath.

(2) The proportion of the energy of the current converted into heat.

(3) The volume of chlorine, at 0°, liberated per minute by a current of 1,000 amperes.

(4) The output of copper in kilograms per kilowatt-hour of electric energy employed.

Solution:

(1) The voltage required includes that necessary to overcome the ohmic resistance of the electrolyte plus that absorbed in chemical decomposition. With a resistivity of 6 ohms, current density 0.5 amperes per square centimeter, and distance between electrodes 4 cm., the first item is

$$V^c = 6 \times 0.5 \times 4 = 12$$

The second item comes from the heat of formation, by dividing that heat expressed per chemical equivalent by 23,040. Since (Cu, Cl) = 35,400 Calories, we have

$$V^d = 35{,}400 \div 23{,}040 = 1.5$$

The total voltage required would be

$$V^c + V^d = \mathbf{13.5} \text{ volts.} \qquad (1)$$

This is independent of drop of voltage at contacts of electrodes with the conductors. That may amount to 0.5 or 1.0 volt, unless the contacts are very closely looked after.

(2) The current drops as sensible heat:

$$12 \div 13.5 = 0.89 = \mathbf{89} \text{ per cent of its energy.} \qquad (2)$$

(3) Assuming 100 per cent efficiency of liberation of chlorine, we have:

Hydrogen gas liberated by 1 ampere, in 1 sec. = 0.00001036 gr.
Chlorine gas liberated by 1 ampere, in 1 sec.
0.00001036×35.5 (Chem. eq. wt.) = 0.0003677 "
Chlorine gas per 1000 amperes in 1 minute = 22.06 "
Volume of chlorine, at 0° C.

$$22.06 \div (0.09 \times 35.5) = \mathbf{6.9} \text{ litres.} \qquad (3)$$

(4) One kilowatt, at 13.5 volts, gives $1000 \div 13.5 = 74$ amperes. This current, in one hour, will furnish, at 100 per cent efficiency

$$2.372 \times 74 = \mathbf{175} \text{ grams of copper.} \qquad (4)$$

Lower current densities would absorb less voltage and give a greater power-factor output.

I. 2—Electrolytic Treatment of Matte.

Matte is a mixture of Cu^2S with FeS, and frequently impure with Pb, Zn, Ag, Au, As, Sb, Ba, etc. It melts sharply at about 1,000° C., to a thin liquid; it sets quickly to a hard, stony mass. When melted it can dissolve copper rapidly, so that electrolysis results in the matte being re-formed as quickly as it tends to be decomposed, and it apparently conducts the current without decomposition. If it could be dissolved in certain other fused sulphides in small amount, such as in fused sodium sulphide, it could conceivably be electrolyzed continuously, but no process has as yet been developed along these lines. If it could be dissolved in aqueous solutions of alkaline or other sulphides, it might be electrolyzed in such solvents, but no successful solvent of this nature has been found. It is not impossible that some aqueous solutions may be found to answer this purpose.

Solid matte is conducting, and may be used as an anode or a cathode. When so used it is acted upon by the electric current, reducingly as cathode and perducingly as anode; that is, used as cathode it tends to be reduced *in situ* to metallic copper and iron, if there is any base present capable of uniting with and carrying away the sulphur; used as anode its copper tends to pass into combination with the acid radicle of the electrolyte, leaving the sulphur behind.

Use of Matte as Anode.

This has appeared to many persons a hopeful application of electrometallurgy to copper. The matte is cast around some strips of copper, or copper netting is better, these giving the piece strength, preventing its disintegrating too quickly, and serving as conductors. Used in acidulated copper sulphate solution, the tendency is to dissolve out copper as copper sulphate and leave the sulphur as a residue. The latter is a non-conductor, forming an insulating layer, which increases greatly the voltage required to run the bath. Attempts to scrape off this layer are fruitless, because of the irregular, cavernous corrosion of the anodes. Marchesi, an Italian, installed a plant to work this process near Genoa in 1882; a plant was also erected in Stolberg, Germany, Both were subsequently abandoned as impracticable.

The theoretical reaction is for purest matte

$$Cu^2S = 2Cu + S$$

so that for four chemical equivalents of copper deposited one molecule of Cu^2S is broken up. The voltage corresponding to the chemical work done is, therefore,

$$\frac{20{,}300 \div 4}{23{,}040} = 0.22 \text{ volt.}$$

The voltage required by the cell is this plus that absorbed in overcoming the ohmic resistances of the circuit.

If the matte were only FeS, the reaction would consist in the solution of iron, sliming of sulphur, and deposition of an equivalent amount of copper:

$$FeS + CuSO^4aq. = Cu + FeSO^4aq. + S$$

and the energies involved are

(Fe, S)	= 24,000	Calories	absorbed
(Cu, S, O^4, aq.)	= 197,500	"	"
(Fe, S, O^4, aq.)	= 234,900	"	evolved
Sum =	13,400	"	"

and the voltage *contributed* to the circuit is

$$\frac{13{,}400 \div 2}{23{,}040} = 0.29 \text{ volt.}$$

If the matte is, as it usually is, part Cu^2S and part FeS, then when it is uniformly corroded there occurs a combination of the above two reactions. If the matte corresponded, for instance, to the formula $Cu^2S.FeS$, and these were simultaneously acted upon, the current would be divided in the proportions required by the preceding reactions; that is, twice as much to handle the Cu^2S as for the FeS. The voltages concerned will enter into the calculation in the proportions 2 to 1, and the calculated voltage of decomposition will be

$0.22 \times \frac{2}{3}$ =	0.147	volt	absorbed.
$0.29 \times \frac{1}{3}$ =	0.097	"	contributed.
Sum =	0.05	"	absorbed.

The calculation can be made for any proportions of Cu^2S and FeS, remembering that every 159.2 parts of Cu^2S require twice as much current as 88 parts of FeS.

Problem 112.

Marchesi erected and operated for some time an electrolytic plant using copper matte as anodes. The matte used contained 30 per cent copper, 30 sulphur and 40 iron, and the anodes measured 800 x 800 x 30 mm., and weighed 125 kilograms. The cathodes were 700 x 700 x 0.3 mm. The tanks were lead lined, with interior dimensions 2,000 x 900 mm. x 1,000 mm. deep. Electrolyte an acid solution of copper and iron sulphates. Resistivity assumed at 6 ohms. The plant contained 120 tanks, arranged in ten groups of twelve each, each group being run by a separate dynamo. Current density, 30 amperes per sq. meter of cathode surface; each tank contained twenty anodes and twenty-one cathodes. Conductors, 30 mm. diameter; total length to one group 10 meters.

Required:

(1) The electrical current required by each group of twelve tanks and the motive power to run its dynamo.

(2) The rate at which the anodes lost weight per day.

(3) The rate at which $FeSO^4$ accumulates in the bath, in per cent of the weight of the bath.

(4) The output of copper per day.

(5) The length of time necessary to plate 1 cm. thickness of copper on one side of each cathode plate.

Solution:

(1) The first point to be solved is the voltage required per tank, and that consists of voltage absorbed by ohmic resistance and that of chemical decomposition. The first must be found from the ohmic resistance of the baths, the second from the chemical reactions involved.

With twenty anodes, each 30 mm. thick, and twenty-one cathodes (the end ones against the ends of the tank) 0.3 mm. thick, the thickness of electrodes in a tank is

$$(20 \times 30) + (21 \times 0.3) = 606.3 \text{ mm.}$$
$$= 60.6 \text{ cm.}$$

and the free space between, in the length of the tank, is

$$200.0 - 60.6 = 139.4 \text{ cm.}$$

Since this is divided into 40 spaces, the free space is

$$139.4 \div 40 = 3.5 \text{ cm.}$$

The total anode surface is, assuming them entirely immersed,

$$80.0 \times 80.0 \times 2 \times 20 = 256{,}000 \text{ sq. cm.}$$

and of the cathodes,

$$70.0 \times 70.0 \times 2 \times 20 = 196{,}000 \text{ sq. cm.}$$

giving current passing through a tank

$$19.6 \times 30 = 588 \text{ amperes.}$$

Since the tank is wider and deeper than the plates, the effective cross-sectional area of electrolyte is 25.6 sq. m. at the anode surface, 19.6 sq. m. at the cathode surface, and greater than either (by spreading of current lines) in between. It will not be far wrong, under these conditions, to take the effective area of the electrolyte as about that of the larger electrode, viz., at 25.6 sq. m. The resistance of the tank thus becomes

$$R = \frac{6 \times 3.5}{256{,}000} = 0.000082 \text{ ohm.}$$

and the voltage absorbed in overcoming ohmic resistance

$$0.000082 \times 588 = 0.048 \text{ volt.}$$

During active corrosion, if copper and iron are dissolved in the proportions 30 to 40, this would be, in chemical equivalent

proportions as $30 \div 31.8$ to $40 \div 28$
or as 0.943 to 1.429

since the current divides, in doing mixed electrolysis, in proportion to the number of chemical equivalents dissolved or deposited. It thus results that $0.943 \div (0.943 + 1.429) = 0.4 =$ 40 per cent of the current is dissolving copper and 60 per cent dissolving iron. The corresponding voltage of the chemical work is, therefore,

$$0.22 \times 0.40 = \quad 0.088$$
$$0.29 \times 0.60 = -\ 0.174$$
$$\text{Sum} = -\ 0.086 \text{ volt.}$$

The sum of these two voltages is

$$V^c = \quad 0.048 \text{ volt}$$
$$V^d = -\ 0.086 \quad \text{“}$$
$$V = -\ 0.038 \quad \text{“}$$

The conclusion is, that as long as the surface of the matte is clean, and no resistance offered by the non-conducting sulphur slime, the bath will really require no outside current to run it, but will practically run itself. The resistance of connections would absorb the small excess of voltage produced. This is as far as calculation can go. Practical experience with the bath records that the voltage required quickly rose to 1 volt, and after a few days running reached 5 volts. It is practically certain that this was caused entirely by the non-conducting film formed on the anodes.

(2) With 588 amps. passing, and 40 per cent dissolving copper, or 235 amps., the copper dissolved per day in one tank is

$$28.46 \times 235 = 6688 \text{ grams}$$
$$= 6.688 \text{ kilograms}$$

and the weight of matte dissolved per day

$$6.688 \div 0.30 = 22.3 \text{ kilograms.}$$

Since the 20 anodes in a tank weigh $20 \times 125 = 2500$ kilograms, their loss of weight per day is

$$22.3 \div 2500 = 0.009 = \mathbf{0.9} \text{ per cent} \qquad (2)$$

and to lose their whole weight would theoretically require

$$100 \div 0.9 = 111 \text{ days.}$$

Practically, the plates went to pieces in about half that time, when about one-half of their weight had been dissolved.

(3) The iron dissolved is 40 per cent of the matte decomposed, or 8.9 kilograms per day. This forms

$$8.9 \times \frac{152}{56} = 24.2 \text{ kg. } FeSO^4.$$

The tank is not quite full of solution, but say to within 3 cm. of the top. This gives a space of

$$200 \times 90 \times 97 = 1{,}746{,}000 \text{ cc.}$$
$$= 1.746 \text{ cu. m.}$$

From this would be deducted the volume of the electrodes:

$$80 \times 80 \times 3 \times 20 = 384{,}000 \text{ cc.}$$
$$70 \times 70 \times 0.3 \times 21 = 34{,}300 \text{ "}$$

$$\text{Sum} = 418{,}300 \text{ "}$$
$$= 0.418 \text{ cu. m.}$$
$$\text{Volume of solution} = 1.328 \text{ "}$$

Assuming its specific gravity as 1.2, the weight of solution in a tank is

$$1{,}328 \times 1.2 = 1594 \text{ kilograms}$$

and its content of $FeSO^4$ is increased per day

$$24.2 \div 1594 = 0.015 = \mathbf{1.5} \text{ per cent.} \quad (3)$$

The total salts present in the electrolyte, however, do not increase quite that fast, for since 16.73 kg. of copper are deposited per day and only 6.67 kg. are dissolved, the electrolyte loses copper at the rate of 10.06 kg. per day, equal to 25.24 kg. of $CuSO^4$ per day, which is 1.6 per cent of the weight of the electrolyte. We may, therefore, say that the electrolyte would lose 1.6 per cent of its weight of $CuSO^4$ per day and gain 1.5 per cent of $FeSO^4$—amounting to a virtual displacement of $CuSO^4$ by $FeSO^4$ until the copper was all removed. This would result in not many days running before the electrolyte would have to be replaced.

(4) We have previously calculated for one tank, that 16.73 kg. of copper is deposited per day. This amounts for the whole plant to

$$16.73 \times 120 = \mathbf{2008} \text{ kilograms.} \quad (4)$$

Of this amount, however, only $6.67 \times 120 = 800$ kg. came from the matte, and the rest from the solution. Ample means

must therefore be provided to supply fresh $CuSO^4$ solution, which was obtained by Marchesi from the roasting and leaching of ore.

(5) Precipitated copper has a density of 8.9. One amp. precipitates per day 28.46 grams. One amp. per square centimeter would therefore deposit in a day

$$\frac{28.46}{8.9} = 3.2 \text{ cubic cm.}$$

$$= 3.2 \text{ cm. thickness.}$$

But the current density used for depositing by Marchesi was only 30 amps. per square meter, = 0.003 amps., per square centimeter, which would deposit a layer per day of

$$3.2 \times 0.003 = 0.0096 \text{ cm.}$$

$$= 0.096 \text{ mm.}$$

To deposit a layer 1 cm. thick would therefore require

$$1.0 \div 0.0096 = \mathbf{104} + \text{days.} \qquad (5)$$

This is a much slower rate of deposition than is used at present in copper refining, where 100 to 500 amps. per square meter (9 to 45 amps. per square foot) are used. Low-current density deposits purer copper and absorbs less power, but gives a smaller output for a given installation, with consequent higher interest charges, labor costs, amortisation and general expenses.

Use of Matte as Cathode.

Pedro G. Salom describes the use of this principle, called by him cathodic reduction, and has applied it on a large scale to the reduction of PbS concentrates, used as cathode in dilute sulphuric acid, to spongy lead. If the process is applied to granulated copper matte, assumed as nearly pure Cu^2S to simplify this discussion, the anode product is O^2 gas, and the cathode product H^2 gas mixed with varying quantities of H^2S. A. T. Weightman (*Transactions American Electrochemical Society*, II (1902), p. 76) gives details of such an experiment.

Problem 113.

Fifteen grams of Cu^2S were used as cathode in a 5 per cent solution of H^2SO^4, using an unattackable antimonial-lead anode. A current of 3.6 amps. was sent through for 3 hours (voltage not given). Area of electrodes 50 sq. cm. each, distance apart 4 cm. Gases contained H^2 and H^2S in the following proportions:

	H^2	H^2S
At 5′	42.4	57.6
At 180′	90.8	9.2
Average 0–180′	79.5	20.5

Required:

(1) The voltage required to run the cell, if H^2S alone were liberated, 100 per cent pure.

(2) The voltage required to run the cell at the beginning, at the end, and the average throughout the run.

(3) The proportion of the Cu^2S reduced to Cu during the run.

Solution:

(1) The voltage to overcome ohmic resistance requires first the resistivity of the electrolyte, which for 5 per cent solution is 4.8 ohms. The ohmic resistance of the cell is, therefore,

$$4.8 \times 4 \div 50 = 0.38 \text{ ohm}$$

and the voltage drop to send 3.6 amperes through this

$$0.38 \times 3.6 = 1.37 \text{ volts.}$$

If H^2S were liberated pure, in which case the solution would be saturated with H^2S, the chemical reactions are

$$Cu^2S + H^2O = 2Cu + H^2S \text{ (gas)} + O$$

and the energy involved

(Cu^2, S)	= 20,300	absorbed
(H^2, O)	= 69,000	"
(H^2, S)	= 4,800	evolved
Sum	= 84,500	absorbed.

The voltage absorbed in producing this chemical reaction is:

$$\frac{84{,}500 \div 2}{23{,}040} = 1.83 \text{ volts}$$

The total voltage necessary to run the cell is

$$1.37+1.83 = \mathbf{3.20} \text{ volts.} \qquad (1)$$

(2) If no H^2S were formed, and the current liberated only H^2 gas, there would be absorbed in decomposition 1.50 volts, and by the cell as a whole 2.87 volts. Since a molecule of H^2S contains the same amount of hydrogen as a molecule of H^2, equal volumes of H^2S or H^2 would be liberated by an equal electric current. It follows, therefore, that at 5 minutes 57.6 per cent of the current was performing reduction, liberating H^2S, and 42.4 per cent liberating hydrogen.

The principle here involved in calculating the voltage dropped corresponding to the chemical work done is that of the composition and resolution of voltages, explained by the writer in *Transactions American Electrochemical Society* V. (1904), p. 89. The numerical result desired may be reached in several ways, for instance,

$$1.83\times0.576 = 1.054$$
$$1.50\times0.424 = 0.636$$
$$V^d = 1.69 \text{ volts.}$$

but, for conduction, $V^c = 1.37$ "

therefore, total voltage $V = \mathbf{3.06}$ "

(2)

At the end of the run we have similarly

$$1.83\times0.092 = 0.168 \text{ volts}$$
$$1.50\times0.908 = 1.362 \text{ "}$$
$$V^d = 1.53 \text{ "}$$
$$V^c = 1.37 \text{ "}$$
$$V = 2.90 \text{ "}$$

(2)

For the average running

$$1.83\times20.5 = 0.375 \text{ volts}$$
$$1.50\times79.5 = 1.193 \text{ "}$$
$$V^d = 1.57 \text{ "}$$
$$V^c = 1.37 \text{ "}$$
$$\mathbf{V = 2.94} \text{ "} \qquad (2)$$

(3) Since 20.5 per cent of the current reduced copper during the run, the weight of copper reduced must have been

$$1.186 \times 3.6 \times 0.205 = 0.88 \text{ grams.}$$

But, the 15 grams Cu^2S contained, if pure,

$$15 \times \frac{127.2}{159.2} = 12 \text{ grams.}$$

Proportion reduced in the three hours

$$\frac{0.88}{12} = 0.073 = \mathbf{7.3} \text{ per cent.} \qquad (3)$$

This method of reduction of matte would need radical improvement before there could be any possibility of its commercial application.

I. 3—Electrolytic Extraction from Solutions.

This branch of the subject covers some promising processes which have not, however, been as yet practically successful. Their consideration, however, from a quantitative point of view, is not devoid of interest or lacking in instruction.

The waters of many copper mines carry copper sulphate, produced from the weathering and leaching of copper sulphide ores. The solutions are generally too dilute to allow of concentration and crystallizing out to blue vitriol. The standard method of treatment is to pass the solutions over pig iron or scrap iron, thus precipitating the copper as a sort of metallic mud called "cement copper," which contains much iron, besides the impurities of the iron used, so that it is sometimes only 90 per cent down to 60 per cent copper. This precipitate needs a strong refining to bring it up to merchant copper, with considerable loss of copper in the operation.

Two electrolytic methods are applicable to the treatment of such solutions: 1. The use of soluble iron anodes. 2. The use of insoluble anodes.

(1). *Use of Soluble Iron Anodes.*

If iron in plates or sheets, or bundles of scrap iron in a crate or holder are immersed in copper sulphate solution and simultaneously connected electrically with a copper plate to serve

as cathode, no copper precipitates on the iron, but all is precipated on the copper. The iron acts as a soluble anode, going into solution as ferrous sulphate, while the copper is deposited out passive, dense, and practically chemically pure, on the cathode sheet. Since more energy is developed by the solution of the iron than is absorbed in the deposition of the copper, there is electromotive force generated by the chemical action, which will run the tank like a short-circuited battery cell, if the iron and copper are simply connected by a low resistance wire. This electromotive force will send a current of a certain amount through the cell, depending on its internal ohmic resistance plus the resistance of the external conductor. If it is desired to force matters, and to precipitate the copper faster than this auto-precipitation, an impressed electromotive force from a dynamo may be put on and the cell made to work faster.

Problem 114.

A copper sulphate solution whose resistivity is 50 ohms is run for precipitation through tanks, each of which contains fifteen anodes of cast iron 40 x 80 cm. in size, and sixteen sheets of copper of similar size, the distance between averaging 5 cm. The anodes and cathodes are short-circuited by resting on a triangular copper distributing bar of negligible resistance. Assume resistance of contacts to be such that 0.1 volt will be lost at them.

Required:

(1) The electromotive force generated by the chemical action.

(2) The total current operative in each tank, and the current density.

(3) The weight of copper deposited in each tank per day.

(4) The weight of iron dissolved in each tank per day.

Solution:

(1) From the thermochemical tables (Metallurgical Calculations, Part I. p. 24) we have:

(Fe, S, O^4, aq.)	= 234,900	Calories
(Cu, S, O^4 aq.)	= 197,500	"
Excess of anode energy =	37,400	"

Since this is generated for each atom of copper deposited and of iron dissolved, the excess energy per chemical equiva-

lent concerned is $37,400 \div 2 = 18,700$ Calories, and the total electromotive force developed is

$$18,700 \div 23,040 = \mathbf{0.81} \text{ volt.} \qquad (1)$$

(2) The loss of voltage at the contacts being 0.1 volt, there is 0.71 volt operative to overcome the ohmic resistance of the solution. From the data given, the fifteen anodes operating on both sides, sandwiched between sixteen cathodes, give

$$15 \times 2 \times 40 \times 80 = 96,000 \text{ sq. cm.}$$

active electrode surface, and taking this as the cross-section of the electrolyte between, we have its resistance as

$$50 \div 96,000 \times 5 = 0.0026 \text{ ohm,}$$

the total current passing in the tank

$$0.71 \div 0.0026 = \mathbf{273} \text{ amperes,} \qquad (2)$$

and the current density

$$\begin{aligned} 273 \div 9.6 &= \mathbf{28.4} \text{ amperes per square meter} \qquad (2) \\ &= \mathbf{2.6} \text{ amperes per square foot.} \end{aligned}$$

(3) Copper deposited in the tank per day:

$$\begin{aligned} 28.46 \times 273 &= 7770 \text{ grams} \\ &= \mathbf{7.77} \text{ kilograms} \\ &= \mathbf{17.13} \text{ pounds.} \qquad (3) \end{aligned}$$

(4) The iron going into solution will be to the copper dissolved as 56 to 63.6. If the iron is cast iron, this may be only 90 to 93 per cent of the loss of weight of the anodes, because they contain only that percentage of iron. If wrought iron or steel sheets are used, the iron dissolved would represent 99 to 99.8 per cent of the loss of weight of the anodes. The iron dissolved per day is

$$\begin{aligned} 7.77 \times 56 \div 63.6 &= \mathbf{6.84} \text{ kilograms} \qquad (4) \\ &= \mathbf{15.08} \text{ pounds.} \end{aligned}$$

Problem 115.

One hundred tanks of the kind described in Problem 114 are arranged in a series, the anodes in each tank, however, connected as one large anode, and the cathodes in each as one

large cathode. A dynamo is connected to the series capable of maintaining 110 volts across its terminals. The bus-bars provided are altogether 280 meters long, and are 1 x 4 cm. in cross-section, of pure copper. All other details of the tanks are as before: resistance of contacts being 0.1 volt ÷ 273 amps. = 0.0004 ohm.

Required:

(1) The ohmic resistance of the bus-bars.

(2) The current operative in the circuit, and the current density.

(3) The weight of copper deposited in each tank per day.

Solution:

(1) The conductivity of copper, in reciprocal ohms, is 600,000; its resistivity $1 \div 600{,}000 = 0.00000167$ ohms. This is its resistance per centimeter cube. The resistance of the bus-bars is therefore

$$0.00000167 \times 28000 \div 4 = \mathbf{0.0117} \text{ ohm.} \qquad (1)$$

(2) The total voltage operative in the circuit is the self-generated voltage of 100 tanks, plus the 110 volts from the dynamo, or

$$(0.81 \times 100) + 110 = 191 \text{ volts.}$$

The total resistance of the circuit is that of the 100 tanks, plus 100 sets of connections, plus that of the bus-bars

$$(0.0026 \times 100) + (0.0004 \times 100) + 0.0117 = 0.3117 \text{ ohm.}$$

The total current flowing will therefore be

$$191 \div 0.3117 = \mathbf{618} \text{ amperes} \qquad (2)$$

and the current density

$$618 \div 9.6 = \mathbf{64.4} \text{ amperes per square meter} \qquad (2)$$
$$= \mathbf{5.9} \text{ amperes per square foot.}$$

$$(3)\ 28.46 \times 618 \div 1000 = \mathbf{17.59} \text{ kilograms per day} \qquad (3)$$
$$= \mathbf{38.79} \text{ pounds per day.}$$

(2). *Use of Insoluble Anodes.*

If insoluble anodes are used, the copper may be extracted *en masse* from such solutions, and its acid left behind. In such operations, the choice of an anode is not easy. Graph-

itized carbon plates are unattacked, and have practically no back electromotive force; high-silicon iron plates are also said to be very resistant, and pure silicon itself resists still better, but introduces considerable ohmic resistance. Sheet lead anodes become coated with a brown coating of PbO^2, which is permanent and evolves oxygen freely. Many other substances may possibly be used as anodes; not many practical results of such tests have been published. When operating thus, the electrolyte offers practically the same ohmic resistance as before, averaging probably a little less, and the chemical reaction absorbs energy. The resulting acidified solution may be utilized for dissolving easily-attacked copper compounds from fresh quantities of raw or roasted ore.

Problem 116.

An electrolytic depositing plant treats dilute copper sulphate solution containing 318 grams of copper per cubic meter as $CuSO^4$, and its copper is deposited by passing through tanks having insoluble anodes, electrodes 3 centimeters apart, and current density of 20 amps. per square meter. With good circulation, copper is precipitated with no evolution of hydrogen until the precipitation is practically complete. By having many tanks in series the current passing is kept very nearly constant at 300 amps. Each tank contains 1.5 cu. m. of electrolyte.

Required:

(1) The voltage absorbed in the chemical reaction when precipitating copper, and when the copper is all precipitated.

(2) The voltage absorbed in overcoming the ohmic resistance of the electrolyte at starting and at the end of the precipitation.

(3) The total voltage across the electrodes of a tank, at the beginning of the precipitation, just before the last of the copper is precipitated and after all copper is precipitated.

(4) The time required to precipitate the copper from a batch of solution.

(5) The output of copper per average kilowatt-hour of electric energy used, adding 0.2 volts to the potential across the electrodes for loss in contacts and bus-bars per tank.

Solution:

(1) When precipitating copper, we destroy $CuSO^4aq.$ and form the corresponding $H^2SO^4aq.$ Their heats of formation being

$(Cu, S, O^4, aq.) = 197{,}500$ Calories
$(H^2, S, O^4, aq.) = 210{,}200$ "

and since the reaction is

$$CuSO^4aq. + H^2O = H^2SO^4aq. + O + Cu$$

we have to supply

$(Cu, S, O^4, aq.) = 197{,}500$ Calories
$(H^2, O) = 69{,}000$ "

Total $= 266{,}500$ "
and get back $(H^2, S, O^4, aq.) = 210{,}200$ "

therefore supplying net $= 56{,}300$ "

and voltage absorbed in decomposition

$$\frac{56{,}300 \div 2}{23{,}040} = \mathbf{1.22} \text{ volts.} \qquad (1)$$

When the copper is all deposited, then only H^2 and O appear at the electrodes, so that the voltage absorbed in decomposition becomes

$$\frac{69{,}000 \div 2}{23{,}040} = \mathbf{1.50} \text{ volts.} \qquad (1)$$

(2) At starting, the solution contains

$$318 \times \frac{159.6}{63.6} = 798 \text{ grams}$$

of $CuSO^4$ per cubic meter, and since the cubic meter weighs at 15° practically the same as water, *i.e.*, 999.1 kg., our solution is

$$\frac{798 \div 1000}{999.1} = 0.08 \text{ per cent } CuSO^4$$

and also equals $0.798 \div \frac{159.6}{2} = 0.01$ normal.

At the end of the electrolysis the 0.01 normal $CuSO^4$ solution becomes a 0.01 normal H^2SO^4 solution. The resistivities of both these solutions can be found at once from electrochemical

tables (*e.g.*, Kohlrausch, in Landolt-Bornstein-Meyerhoffer's Tabellen).

With a current density of 20 amps. per square meter (0.002 per square centimeter) and a working distance of 3 cm., the corresponding voltages absorbed in overcoming these ohmic resistances will be

$$1395 \times 3 \times 0.002 = \mathbf{8.37} \text{ volts}$$
$$325 \times 3 \times 0.002 = \mathbf{1.95} \text{ "} \qquad (2)$$

(3) The total voltage across the electrodes, assuming the solution to contain no free acid at starting, will be

at start, precipitating copper: $8.37 + 1.22 = \mathbf{9.59}$ volts
at close, precipitating last copper: $1.95 + 1.22 = \mathbf{3.17}$ "
at close, evolving hydrogen: $1.95 + 1.50 = \mathbf{3.45}$ "

(4) Copper present in a tank: $318 \times 1.5 = 477$ grams.
Time required, 300 amperes

$$477 \div (300 \times 0.0003295) = 4826 \text{ seconds}$$
$$= \mathbf{1 \text{ hr. } 20.5 \text{ min.}} \quad (4)$$

(4) The average voltage consumed in overcoming ohmic resistance will be considerably less than the mean of 8.37 and 1.95 = 5.16 volts, because when the electrolysis is only half completed, and the solution is 0.005 normal in each ingredient, its resistance will be 487 ohms, and not $(1{,}395 + 325) \div 2 =$ 860 ohms, and the corresponding voltage 2.92. This is because sulphuric acid is a so much better conductor than $CuSO^4$, that as soon as acid forms the solution becomes much better conducting. If we calculate the resistances and corresponding voltages absorbed in several steps, we would get more accurate results. Without going into the detailed calculation we will take 3.52 as the average voltage, and we then have the average voltage required per tank:

Decomposition	1.22 volts
Resistance	3.52 "
Contacts	0.20 "
Sum	4.94 "

Kilowatts used per tank

$$\frac{4.94 \times 300}{1000} = 1.482 \text{ kw.}$$

Output per tank per hour

$$300 \times 1.186 = 355.8 \text{ grams.}$$

Output per kilowatt-hour

$$355.8 \div 1.482 = 240 \text{ grams.} \quad (4)$$

This is, of course, a small output compared with that of a refining process, but it must be remembered that this is an *extraction* process, and its cost is not properly comparable with simple refining but with that of the processes which it replaces, such as precipitation by iron, and with cheap power and expensive iron there may be localities where this method would be economical.

Siemens and Halske invented a combined wet-extraction and electrolytic process, consisting in leaching the roasted copper ore or matte with a solution of ferric sulphate acidulated with sulphuric acid, producing thus a solution of cupric and ferrous sulphates, and then electrolyzing this solution in a cell having an insoluble carbon anode and a diaphragm between the electrodes. The solution is run first through the series of cathode compartments, where its copper is extracted, and back through the anode compartments, where its ferrous sulphate is perduced to ferric sulphate, ready to be used again in leaching ore.

The chemical reactions in leaching ore are

$$Cu^2S + 2Fe^2(SO^4)^3aq. = 2CuSO^4aq. + 4FeSO^4aq. + S.$$
$$3CuO + Fe^2(SO^4)^3aq. = 3CuSO^4aq. + Fe^2O^3.$$
$$CuO + H^2SO^4aq. = CuSO^4aq. + H^2O.$$

In the electrical precipitation we have:

in the cathode compartments: $CuSO^4 = Cu + SO^4$
in the anode compartments: $2FeSO^4 + SO^4 = Fe^2(SO^4)^3$
altogether: $2FeSO^4 + CuSO^4 = Cu + Fe^2(SO^4)^3$

Confining our calculations to the electrolysis, we have $CuSO^4$ destroyed and $2FeSO^4$ simultaneously perduced to $Fe^2(SO^4)^3$, which is then available for re-use in the leaching tanks. The chemical work involved is:

$(Cu, S, O^4, aq.)$	= 197,500	Calories	absorbed
$2(Fe, S, O^4, aq.)$	= 469,800	"	
$(Fe^2, S^3, O^{12}, aq.)$	= 650,500	"	evolved
Sum =	16,800	"	absorbed

$$\text{Voltage thus absorbed} = \frac{16{,}800 \div 2}{23{,}040} = 0.36 \text{ volt.}$$

In addition to this, the voltage necessary to overcome the ohmic resistance of the cell must be counted in.

Problem 117.

An electrolytic tank for working the Siemens-Halske method was of wood, lead lined, 220 cm. long, 100 cm. wide and 100 cm. deep. Each cell contained fifteen anodes and sixteen cathodes, the latter 80 x 80 cm. x 1 mm. The anodes were of carbon rods arranged as a grid 45 cm. x 100 cm. x 1 cm. thick. A porous partition 1 cm. thick was used, the *equivalent* effective free area of which was 0.05. Resistivity of electrolyte in cathode compartment 5 ohms, in anode compartment 8 ohms, partition in middle. Current density 100 amperes per square meter.

Required:

(1) The distance between the diaphragm and each anode and cathode surface, and the resistance of the cell, taking into consideration the contraction of current path due to the diaphragm.

(2) The voltage necessary to run the tank.

Solution:

(1)

15 anodes $\times$ 1	=	15.0 cm.
16 cathodes $\times$ 0.1	=	1.6 "
	Sum =	16.6 "

Space, anode to cathode

$$\frac{220 - 16.6}{30} = 6.8 \text{ cm.}$$

Space, anode or cathode, to diaphragm

$$\frac{6.8 - 1}{2} = 2.9 \text{ cm.} \qquad (1)$$

Assume the solution in the diaphragm to have mean resistivity of 6.5 ohms, the equivalent free area being $100 \times 95 \times 0.05 = 475$ sq. cm. (area of diaphragm a trifle less than cross-section of tank). Mean area of electrolyte

cathode compartment	$(6400+9500)\div 2$	= 7950 sq. cm.
anode compartment	$(4500+9500)\div 2$	= 7000 " "
Resistance of		
anode compartment	$8\times 2.9\div 7000$	= 0.0033 ohm.
cathode compartment	$5\times 2.9\div 7950$	= 0.0018 "
diaphragm	$6.5\times 1\div 475$	= 0.0137 "
		0.0188 " (1)

Voltage absorbed, for 64 amperes (to 0.64 sq. m. depositing surface)

0.0188×64	= 1.20 volts	
V^d	= 0.36 "	
V	= **1.56** "	(2)

Carl Hoepfner devised a process along similar lines to the above, but based on the use of the two chlorides of copper. A solution of $CuCl^2$ in brine is used to act upon the ores or roasted matte, dissolving the copper with the formation of CuCl.

$$2CuCl^2+Cu^2S = 4CuCl+S.$$

The cuprous chloride stays in solution in the brine, and is electrolyzed in tanks containing diaphragms, half the solution going through the cathode compartments, and half through the anode compartments. In the former, copper is precipitated; in the latter, the equivalent amount of chlorine converts the CuCl present into $CuCl^2$, which can be used over, mixed with the depleted cathode solution. The total reaction is

$$CuCl+CuCl = Cu+CuCl^2$$

and the energy involved

2(Cu, Cl)	= 70,800 absorbed
(Cu, Cl^2)	= 62,500 evolved
Sum	= 8,300 absorbed
	= **0.18** volt.

Coehn devised a cell for carrying on this process without a diaphragm. The cathode is only half as long as the carbon anode, and the $CuCl^2$ formed at the latter is so heavy that it sinks to the bottom and is drawn off therefrom, while fresh CuCl solution is quietly poured in above. Since the cathode

does not touch the cupric solution, it is not redissolved thereby, and the two solutions are kept separate.

A great advantage of this process is that Cu is monovalent in CuCl, and therefore twice as much copper is deposited as from $CuSO^4$ by a given number of amperes.

Problem 118.

Coehn (*Jahrbuch der Electrochemie*, 1895, p. 155) describes his improved partitionless Hoepfner apparatus as containing a copper cathode 100 cm. wide by 50 cm. deep, at a distance of 12 cm. from a carbon anode; solution, 10 per cent NaCl, plus varying amounts of CuCl and $CuCl^2$. Current density 20 amps. per square meter.

Required:

(1) The voltage required to run the cell.

(2) The weight of copper deposited therein per day.

(3) The weight of copper per kilowatt hour electric power used.

Solution:

(1) The resistivity of 10 per cent NaCl solution is 8.5 ohms.

$$R = \frac{8.5 \times 12}{5000} = 0.0204 \text{ ohm}$$

V^c, for ohmic resistance $= 0.0204 \times 10 = 0.20$ volt

V^d, for chemical reactions 0.18 "

$V = \text{Sum} = \mathbf{0.38}$ " (1)

(2) $28.46 \times 2 \times 10 = \mathbf{569}$ grams per day (2)

(3) $\frac{569}{24} \times \frac{1000}{10 \times 0.38} = \mathbf{6210}$ grams

$= \mathbf{6.21}$ kg. (3)

I. 4. Electrolytic Refining of Impure Copper.

This subject is a large one. It lends itself very well to calculation. It is also comparatively simple in principle. Given a nearly pure copper plate or slab as an anode, in a solution of a copper salt, and a suitable conducting cathode, the metal is simply dissolved and deposited, or is "plated over." The process really consists in extracting copper from the solution at the cathode, and sending it and other soluble impurities into the solution at the anode. The mechanical transportation of the copper, in space, through a distance equal to the space between anode and cathode, is sometimes emphasized as the chief

mechanical work done. It is a real fact that the metal is taken out of the solution at a different spot from where it goes in, but the electric current does not do that transportation—diffusion and circulation are the agents which transport the copper entering the electrolyte at the surface of the anode plate to the surface of the cathode plate, and electric energy does nothing more than create the differences of concentration, which are thus physically neutralized.

The chief expenditure of electrical energy in the refining bath is that converted into sensible heat in overcoming the ohmic resistance of the electrolyte. The other items of electrical work are the overcoming of the ohmic resistance of hangers. rods, bus-bars, clamps and connectors, and the not unimportant resistance of contacts; also the difference of chemical work done in depositing all copper and dissolving part copper and part other impurities; also the chemical work of separating the ingredients of the impure copper, which may be alloyed and have some heat of combination which must be furnished by the current in order to separate them.

Energy Absorbed by the Electrolyte.

The electrolyte is a conductor and absorbs energy according to Ohm's law whenever current passes through it. The solution used in copper refining is almost invariably copper sulphate acidulated with sulphuric acid. The resistivity of copper sulphate, iron sulphate and sulphuric acid solutions, at 20° C., is as follows, in ohms per centimeter cube and ohms per inch cube:

Per Cent	*$CuSO^4$.*		*$FeSO^4$.*		*H^2SO^4.*	
in	*Ω per*	*Ω per*	*Ω per*	*Ω per*	*Ω per*	*Ω per*
Solution.	*$cm.^3$*	*$inch^3$.*	*cm^3.*	*$inch^3$.*	*cm^3.*	*$inch^3$.*
2.5	92	37	..	..	....	....
5.	53	21	..	..	4.8	1.9
7.5	..	..	65	26	....	....
10.	31	12	..	..	2.5	1.0
15.	24	10	34	14	1.8	0.7
17.5	22	9	..	..	....	....
20.	..	..	..	..	1.5	0.6
25.	..	..	..	..	1.4	0.56
30.	..	..	25	10	1.37	0.55

The plain copper sulphate solution is thus seen to be a rather poor conductor, iron sulphate is not so good; sulphuric acid is highly conducting. It is therefore evident that the ohmic resistance of the bath is, for practical purposes, dependent upon its content in free acid; hence the great economic importance of keeping the bath well acidulated. As the bath grows foul with iron sulphate and loses sulphuric acid by formation of insoluble sulphates, chemical solution of slimes, etc., the bath becomes poorer conducting and the energy absorbed in it much greater. A solution in good condition, with 15 to 20 per cent of $CuSO^4$ and 5 to 10 per cent free H^2SO^4, may have a resistivity of only 2 to 5 ohms at starting, which may increase to 20 or 25 ohms as the solution becomes impure and the free acid disappears. These facts are of immense importance in the economics of refining.

A comprehensive, systematic study of the resistivities of solutions of various strengths of copper sulphate with various percentages of iron sulphate present and various content of sulphuric acid is greatly needed, and would not be a difficult research to carry out.

Problem 119.

A refining bath is run with a current density of 250 amperes per square meter, with electrodes 4 cm. apart, and starting with electrolyte 15 per cent $CuSO^4$ and 10 per cent H^2SO^4. It is run until the sulphuric acid has decreased to 5 per cent.

Required:

(1) The probable voltage drop across the electrodes at starting.

(2) The same when the second condition is reached.

(3) The rate at which the solution would start to rise in temperature at the beginning, ignoring the electrodes.

(4) The rate, assuming anodes 5 cm. thick and copper cathodes 0.5 cm. thick.

Solution:

(1) Lacking the experimentally determined datum of the resistivity of the primary solution, we know that it will be somewhere about that of the 10 per cent sulphuric acid solution, viz.: 2.5 ohms. It should be slightly less, because of the copper salt present, and if we assume the conductivity of the solutions

as additive, we would have a conductivity of the mixed solution, in reciprocal ohms as

$$C = \frac{1}{2.5} + \frac{1}{24} = 0.40 + 0.04 = 0.44$$

$$R_{sp} = \frac{1}{0.44} = 2.3 \text{ ohms.}$$

Using this resistivity, the voltage drop across the electrodes, at starting, will be

$$V^c = 2.3 \times 4 \times 0.0250 = \mathbf{0.23} \text{ volts.} \qquad (1)$$

(0.0250 amperes goes across each square centimeter and the plates are 4 centimeters apart.)

(2) With H^2SO^4 only 5 per cent, and copper contents, say, 20 per cent, because of solution of copper by free acid, we would have

$$C = \frac{1}{4.8} + \frac{1}{20} = 0.21 + 0.05 = 0.26$$

$$R_{sp} = \frac{1}{0.26} = 3.6 \text{ ohms.}$$

Using this resistivity, the voltage drop is

$$V^c = 3.6 \times 4 \times 0.0250 = \mathbf{0.36} \text{ volts.} \qquad (2)$$

In actual practice an increase of 0.01 volt above this might be expected, because of the formation of a film of slime on the surface of the anode.

(3) The solution at starting has a specific gravity of 1.20 and a specific heat of 0.875. (Combination of data from Landolt-Bornstein-Meyerhoffer's Tabellen.) The water value as heat absorber of a column of liquid 1 cm.^{2} and 4 cm. long, between the electrodes, is therefore

$$1.20 \times 4 \times 0.875 = 4.2 \text{ calories per } 1^\circ \text{ C.}$$

Heat equivalent of the electric energy expended

$$0.23 \times 0.0250 \times 0.2389 = 0.00138 \text{ calories per } 1''.$$

Rate of rise of temperature of solution

$$\begin{aligned} 0.00138 \div 4.2 &= 0.00033^\circ \text{ per second} \\ &= 0.0198^\circ \quad \text{“ minute} \\ &= \mathbf{1.2^\circ} \quad \text{“ hour} \\ &= \mathbf{28.8^\circ} \quad \text{“ day} \end{aligned} \tag{3}$$

(4) With half the thickness of anode and cathode to be supplied with heat, the copper having a specific gravity of 8.9 and specific heat of 0.093, the water value of the copper concerned per square centimeter area of electrolyte section is

$$\left(\frac{5.0}{2}+\frac{0.5}{2}\right)\times 8.9\times 0.093 = 2.276 \text{ calories per } 1^\circ$$

Rate of rise of temperature of solution plus electrodes:

$$\begin{aligned} 0.00138 \div (2.276+4.2) &= 0.00021^\circ \text{ per second} \\ &= 0.013^\circ \quad \text{“ minute} \\ &= 0.78^\circ \quad \text{“ hour} \\ &= \mathbf{18.7^\circ} \quad \text{“ day} \end{aligned} \tag{4}$$

Energy Lost in Contacts.

This is an extremely variable and yet important factor in the economics of copper refining. No one item in copper refining will at the present time better repay close attention and study of methods of improvement. A proper contact should cause a very small voltage drop to begin with, and should be capable of being kept efficient—that is the chief requirement. Contacts are often made on the hit or miss style, and arranged in such position as to receive spattering or drippings from the electrolyte; such may cause immense losses of electrical energy as they rapidly pass from bad to worse.

B. Magnus (*Electrochemical and Metallurgical Industry*, December, 1903), and L. Addicks (*idem.*, January, 1904) have given us valuable information on this point. The weight of the plates, when resting on the contacts, improves the contact; in such cases the anode contacts are best when the tank is first set up and the cathode contacts worst. In such cases a screw clamp, to put several hundred pounds of mechanically applied pressure on the joint, should be adopted, so as to make the contacts “ best ” all the time.

Figures given by Magnus as a carefully determined average of results in a western refinery are:

Current	4,000 amperes		
Current density (per sq. ft.)	11 "		
Total voltage per tank	0.230 volts		
Energy used per tank	0.920 kw.		*Per Cent.*
Drop bus-bar to anode rod	0.0270 volts	= 0.0338 =	14.7
" anode rod to anode hanger	0.0060 "		
" anode hook to anode	0.0008 "		
" anode to cathode	0.1782 "	= 0.1782 =	77.5
" cathode to cathode rod	0.0045 "	= 0.0180 =	7.8
" cathode rod to bus-bar	0.0135 "		
		0.2300	100.0

It thus appears that in this tank the loss in contacts was some 20 per cent of the total voltage employed (assuming the anode rods to be of such design that their resistance was negligible). Magnus fitted up a similar tank with mercury cup contacts, and found a drop from bus-bar to anode rod of 0.0050 volt instead of 0.0270, and cathode rod to bus-bar 0.0050 instead of 0.0135 volt. If it were possible in the case of above tank to make these improvements alone, the saving on voltage per tank would be 0.0305 volt, or 13.3 per cent of the voltage used, which means a saving of 13.3 per cent of the power required to run the tank.

Problem 120.

In an electrolytic refinery system of 200 tanks the resistance of the contacts was, on an average, 0.0368 volt per tank, and 0.2567 volt across two electrodes; 3,800 amperes was passed through the series, and the voltage at the terminals of the dynamo was 67 volts. Power costs $157 per kilowatt-year, Efficiency of deposition of copper 82 per cent.

Required:

(1) The cost of power per ton (2,000 pounds) of copper refined.

(2) The cost per ton of copper produced, of the power lost

by (a), resistance of the conductor bars (b), by the contacts and (c), consumed in the electrolyte itself.

(3) If interest on capital is 6 per cent, what expenditure would be justified on means for (a), reducing the conductor losses (b), reducing the contact losses (c), reducing the electrolyte losses.

(4) If the ampere efficiency of deposition could be increased 5 per cent by reducing the current density 20 per cent, would it pay?

Solution:

(1) Copper deposited in 1 tank per day

$$3800 \times 0.82 = 3118 \text{ oz.} = 195 \text{ lbs.}$$

In 200 tanks

$$200 \times 195 = 39{,}000 \text{ "}$$

Power used

$$3800 \times 67 \div 1000 = 255 \text{ kw.}$$

Cost of power per day

$$255 \times \$157 \div 365 = \$109.70$$

Cost of power per 2,000 lbs. copper

$$\$109.70 \div 19.5 = \mathbf{\$5.63} \qquad (1)$$

(2) The voltage lost in the conductors is

$$67 - 200(0.0368 + 0.2567) = 67 - 58.7 = 8.3 \text{ volts}$$

and the power thus lost

$$3800 \times 8.3 \div 1000 = 31.54 \text{ kw.}$$

Cost per year $31.54 \times \$157 = \$4{,}952.00$

Cost per day $\$4952 \div 365 = \$13.57$

Cost per ton of copper produced = **\$0.70** (2*a*)

Power lost in the contacts

$$200 \times 0.0368 \times 3800 \div 1000 = 27.97 \text{ kw.}$$

Cost, per year = \$4,391.00

Cost, per day = \$12.03

Cost, per ton = **\$0.62** (2*b*)

Power consumed in the electrolyte

$$200 \times 0.2567 \times 3800 \div 1000 = 195 \text{ kw.}$$

Cost, per year = \$30,615.00

Cost, per day = \$83.88

Cost, per ton = **\$4.30** (3*b*)

(3) The cost of the power lost per year, divided by 0.06, will give the capital investment representing that yearly outlay. This would be

	Cost of Power	*Capitalized.*
Conductor resistances.....	$4,952	$82,530
Contact resistances.....	4,391	73,180
Electrolyte resistances.....	30,615	510,250

In the specific cases in point each 1 per cent of the power consumption which could be saved by improvements of a permanent character, not subject to depreciation, would justify capital expenditures in the plant up to the following amounts:

Conductor resistances.....	$825
Contact resistances.....	732
Electrolyte resistances.....	5,100

If the improvements were liable to depreciation in use, such as larger tanks, contact clamps, etc., the depreciation must be added to the interest to find the justifiable capital expenditure. Assuming depreciation 10 and 20 per cent, respectively, this plus interest amounts to 16 and 26 per cent, and the justified expenditures must be less than the following amounts for 1 per cent saving of power in each direction:

	10% *Depreciation.*	20% *Depreciation.*
Conductor resistances.....	$309.50	$190.50
Contact resistances.....	274.50	169.00
Electrolyte resistances.....	1,913.50	736.00

There is here a wide field for experiment and improvement. In the case in point, making all allowances, one would be justified in expending in permanent plant for each tank at least $1.00 for every 1 per cent reduction which could be made in the power loss in the conductors, $0.85 for every 1 per cent gained in reducing contact resistances and $3.68 for each 1 per cent reduction in the resistance of the electrolyte. To be more specific, assume the main conductors to be proportioned to carry 2,000 amperes per square inch of cross-section. Their resistance in the case in point is $8.3 \div 3{,}800 = 0.0022$ ohm, cross-section 1.9 square inches, resistance per running inch $0.00000067 \div 1.9 = 0.00000035$ ohm, and total length $0.0022 \div 0.00000035 = 6{,}286$ inches = 524 feet.

The weight, at $62.5 \times 8.9 \div 1{,}728 = 0.322$ lbs. per cubic inch is

$$6{,}286 \times 1.9 \times 0.322 = 3{,}846 \text{ lbs.}$$

which at \$0.20 per lb. costs

$$3{,}846 \times 0.20 = \$769.20$$

Since there is practically no depreciation (except change in market value) in these copper conductors, if we increased the cross-section of the conductors 100, 200, 300, and 400 per cent, respectively, we would decrease their resistance 50, 67, 75 and 80 per cent, respectively, and arrive at the following figures:

		Per Ton of Copper Produced.			
Per Cent Increased Size of Conductors.	*Per Cent Decreased Resistance of Conductors.*	*Increased Cost of Plant.*	*Interest on Increased Cost of Plant.*	*Decreased Cost of Power.*	*Gain.*
100	50	\$769	\$0.0065	\$0.35	\$0.35
200	67	1,538	0.013	0.47	0.46
300	75	2,307	0.019	0.52	0.50
400	80	3,077	0.026	0.56	0.53
900	90	6,923	0.058	0.63	0.57
1,900	95	14,613	0.123	0.67	0.54

We thus see that for this plant, with power costing \$157 a kilowatt-year and copper bar \$0.20 per pound, a great reduction in the power costs up to \$0.57 per ton of copper produced can be made by making the main conductors *ten times* as large; that is, by making them carry only 200 amperes per square inch of section instead of 2,000.

At a locality like Great Falls, Montana, where the water power does not cost over one-tenth the above price, let us say \$15.70 per kilowatt-year, the decreased cost of power, in the above table would be one-tenth the above figures—there would be only \$0.07 per ton of copper to save if all were saved, and it can easily be seen that the gains would be

for 100 per cent increased size.....	\$0.029
" 200 " " "	0.034
" 300 " " "	0.033
" 400 " " "	0.030

We reach the maximum saving in this case by increasing the size 200 per cent, giving a current density of 660 amperes per square inch of conductor section.

It can easily be seen that the cost of copper bars, rate of interest, and cost of power are all three factors in determining the economic size to be given the conductors. In general they are made much smaller than they should be because of lack of capital to invest in them. As soon as a refinery is running and paying dividends part of its profits should be applied to permanent investment in heavier copper conductors in order to reduce the running costs.

(4) If the ampere efficiency were increased 5 per cent and the current density 20 per cent, all other data being constant except those affected by these changes, the output of copper would be 87 per cent of the theoretical output of 3,040 amperes instead of 82 per cent of the theoretical output of 3,800 amperes. The output of copper per day would therefore be, in place of 39,000 pounds:

$$3{,}040 \times 0.87 \times 200 \div 16 = 33{,}060 \text{ lbs. per day.}$$

The power cost will be reduced 20 per cent by the lower amperage used, that is, be $\$5.63 \times 0.80 = \$4.50$ per ton—a saving of $1.13. Whether it will pay to do this depends of what the other fixed charges of the plant are. Decreasing the output 15 per cent increases the fixed charges per ton of copper produced 12 per cent. It is then a question whether 12 per cent of the fixed charges in the first case is greater or less than $1.13. If the fixed charges amounted to, say, a usual figure of $5.00 per ton, decreasing the output 15 per cent would increase this charge per ton of copper produced 12 per cent, or $0.60; but if there is a power saving of $1.13 there is a margin of $0.53 per ton in favor of making the change. If the power cost were only $0.56 per ton of copper it would just barely pay to make the change. Everything depends upon the relative cost of power and of the other fixed charges.

Energy Lost in Conductors.

We have already touched on this subject, but it deserves still greater attention. The resistivity of copper is 0.00000167 ohm per centimeter cube, or 0.00000067 ohm per inch cube.

Given a conductor of certain length its resistance in ohms is 0.00000167 multiplied by its length in centimeters and divided by its cross sectional area in square centimeters. The similar calculation can be made, for the inch units. The drop in potential in the bus-bars is their resistance multiplied by the amperes passing, and the power consumption is the voltage drop into the amperes passing or the resistance in ohms into the square of the amperes passing. The watts thus expended may be expressed in kilowatts, or transposed into horse-power by dividing by 746. The heat generated in the conductors is, per second, in gram calories, the number of watts expended in them multiplied by 0.2389. The rate of rise of temperature of the conductors, leaving out radiation and conduction to the air, will be, per second, the gram calories generated in the conductors divided by the heat capacity of the conductors per degree, which in the case of copper is volume in cubic centimeters into 0.837. This rise in temperature will continue until by radiation and conduction to the air the conductors lose as much heat per second as the current generates in them. This will vary with the shape of the cross section of the conductors, because the loss of heat is proportional to the surface exposed, and the area of exposed surface for a given cross section is greater the thinner the conductor and is a minimum for a round conductor. The amount of heat thus lost can be calculated by the principles explained in Metallurgical Calculations, Part I., pp. 172–186. If it is desired to get along with the minimum heating of the conductors, they should be as flat and thin as possible; if heating can be ignored they may be of the cheap round shape. It should not be forgotten also that the resistivity of copper increases as it gets hotter in direct proportion to its absolute temperature (C° + 273), so that the heating effect really aggravates itself from this increased resistance.

Problem 121.

A copper conductor is desired to carry 4,000 amperes, 300 meters. Round bars sell at 18 cents per pound. Interest rate 10 per cent. Cost of electric power as delivered $50 per kilowatt year. Average temperature of surrounding air 20° C.; air still. Conductivity of the copper 600,000 reciprocal ohms per centimeter cube. Specific gravity of copper 8.9, specific heat 0.094.

Aluminium conductors to replace same have conductivity of 375,000 reciprocal ohms, specific gravity 2.60, specific heat 0.230; cost of round bars 36 cents per pound.

Required:

(1) The cross-sectional area of the conductors of copper which will give the minimum cost of power and interest on the investment.

(2) The same for aluminium.

(3) The running temperature of the conductors of copper above the room temperature.

(4) The same for aluminium.

Solution:

(1) Let S = cross section of conductor, in sq. cm.

Resistance of copper conductor

$$0.00000167 \times (300 \times 100) \div S = \frac{0.0501}{S} \text{ ohm.}$$

Power expended in the conductor:

$$\frac{0.0501}{S} \times (4{,}000)^2 = \frac{801{,}600}{S} \text{watts.}$$

Cost of power thus expended, per year

$$\frac{801{,}600}{S} \div 1{,}000 \times 50 = \frac{40{,}080}{S} \text{ dollars.}$$

Weight of copper in conductor:

$$(300 \times 100) \times S \times 8.9 \div 1{,}000 = 267 \times S \text{ kilograms.}$$

Cost of conductor, if round

$$267.\ S \times 0.18 \times 2.205 = 106 \times S \text{ dollars.}$$

Interest on cost of conductor, at 10% $= 10.6 \times S$ dollars.

Sum of cost of power and interest on investment:

$$\frac{40{,}080}{S} + (10.6 \times S)$$

Solving for S a minimum, we find $S = \mathbf{61.5}$ **sq. cm.** (1)

Total costs, substituting S above

\$652 (for power) + \$652 (interest) = \$1,304 per year.

(2) Resistance of aluminium conductor

$$0.00000267 \times (300 \times 100) \div S = \frac{0.0801}{S} \text{ ohm.}$$

Power expended in the conductor

$$\frac{0.0801}{S} \times (4{,}000)^2 = \frac{1{,}281{,}600}{S} \text{ watts.}$$

Cost of power thus expended, per year

$$\frac{1{,}281{,}600}{S} \div 1{,}000 \times 50 = \frac{64{,}080}{S} \text{ dollars.}$$

Weight of aluminium in conductor

$$(300 \times 100) \times S \times 2.6 \div 1{,}000 = 78 \times S. \text{ kilograms.}$$

Cost of conductor, if round

$$78.\ S. \times 0.36 \times 2.205 = 62 \times S. \text{ dollars.}$$

Interest on cost of conductor, at 10% $= 6.2 \times S.$ dollars.

Sum of cost of power and interest on investment:

$$\frac{64{,}080}{S} + (6.2 \times S.)$$

Solving for S = a minimum: S = **101.2** sq. cm. (2)

Total costs, substituting S above

$633 (for power) + $627 (interest) = $1,260 per year.

(3) Power expended in copper conductor

$$\frac{801{,}600}{61.5} = 13{,}035 \text{ watts.}$$

Heat generated in conductor, per second

$$13{,}035 \times 0.2389 = 3{,}114 \text{ gm. cal.}$$

Area of conductor surface

$$(300 \times 100) \times 3.14\ (\sqrt{61.5} \div 0.7854) =$$
$$= 30{,}000 \times 27.8 \text{ (cm. circumference)} = 834{,}000 \text{ sq. cm.}$$

Loss of heat per second by contact with still air, per 1° difference

$$0.000056 \times 834{,}000 = 46.7 \text{ calories.}$$

Rise of temperature, excluding radiation loss

$$3{,}114 \div 46.7 = 67°.$$

The radiation loss must, however, be considered. From copper it is 0.00068 gram calories per second per sq. centimeter, if the surroundings are at 0° and the hot body at 100°, this is approximately 0.0000068 gram calories per each degree in this range. We have the combined conduction and radiation losses per 1° per second

$$0.000056 + 0.000007 = 0.000063 \text{ calories}$$

and the rise in temperature of the conductor

$$3{,}114 \div (0.000063 \times 834{,}000) = 59°.$$

The conductors would therefore run at a temperature of

$$\begin{aligned} 20 + 59 &= 79° \text{ C.} \\ &= 174° \text{ F.} \end{aligned} \qquad (3)$$

A correction of the second order would be to take into consideration the fact that at 79° the copper would have less conductivity than at 20°, its resistivity at 79° being

$$0.00000167 \times \frac{273+79}{273+20} = 0.0000020 \text{ ohm.}$$

This would make the required section for minimum expense 68 sq. cm. instead of 61.5, and would, by increasing the surface, make a different rise in temperature. The power expended would be the equivalent of 3,373 gram calories per second, and the revised temperature of the conductor would be

$$(3{,}373 \div 52.54) + 20 = 64 + 20 = 84° \text{ C.}$$

(4) Power expended in the aluminium conductor

$$\frac{1{,}281{,}600}{101.2} = 12{,}665 \text{ watts.}$$

Heat generated in conductor, per second

$$12{,}665 \times 0.2389 = 3{,}026 \text{ calories.}$$

Area of conductor in square centimeters = 1,074,000 sq. cm.

Conduction and radiation losses, per 1°

$$(0.000056+0.000010)\times 1{,}074{,}000 = 70.88 \text{ grm. cal.}$$

Rise in temperature of conductor

$$3{,}026 \div 70.88 = 43°.$$

Working temperature of conductor

$$43+20 = 63° \text{ C.}$$

The aluminium conductor thus is seen to work cooler than the copper, and to admit of a lower minimum of working costs.

Electric Smelting of Copper Ores.

The use of electrothermal processes for smelting copper ores has been proposed in recent years, and in a few cases experimentally tested. The whole question depends on the recognition and appreciation of a few fundamental facts. By far the greater bulk of all copper ores are sulphide ores, and in many cases the sulphur and iron present are sufficient heat producers to allow of the smelting of the ore simply by the heat of their oxidation, if the operation is skillfully conducted. Such is the basic principle of pyritic smelting, and whenever it can be applied it is very economical to do so, and electric processes have no chance of an application.

Other ores of copper contain so small an amount of the metal that the result of the smelting down of the whole to a fluid mass, by any method of fusion, would not repay the cost of the operation. Some such ores can be treated by aqueous and other methods not involving fusion, with a margin of profit to pay for the operation.

The only field for electrothermic processes appears to be in the smelting down of ores carrying too little sulphur to be "pyritically" smelted, and which require, as usually treated, the use of carbonaceous fuel to assist the fusion. Wherever such fuel is expensive, and electric power may be obtained at a low price, an electrothermic process might be theoretically possible and profitable.

Such conditions may easily occur in the vicinity of copper mines. Situated frequently among the mountains, remote from

railways and cheap fuel, they frequently are near large water powers which would furnish cheap electric power. Some may be even so situated that concentration of a very lean sulphide ore to matte by use of fuel, or by mechanical concentration, would be unprofitable, and yet a concentration or simple melting to matte by electrically-generated heat be profitable.

There are, so far as the writer knows, no electrothermal processes yet in commercial operation on copper ores, yet they have been tested experimentally with promising results. Vattier, for instance, conducted experiments at the Livet works of the Compagnie Electrothermique Keller et Leleux, on April 23, 1903, in the presence of several distinguished metallurgists, such as Mr. Stead, of Middlesborough; Mr. Allen, of Sheffield, and Mr. Saladin, of the Creusot works. The ores were Chilian ores sent by the Chilian Government to test the possibility of electric smelting, taken from the " Vulcan " mine, owned by G. Denoso, and low-grade ore from Santiago. At the mines, coke costs $20 per ton, but the slopes of the Andes afford a fine opportunity for developing large water powers cheaply; it is estimated that the total cost of electric power delivered should not exceed $6 per kilowatt-year. A detailed account of these tests can be found in the appendix to the Report of the Canadian Commission on Electric Smelting, 1904.

Problem 122.

Vattier mixed his rich and poor Chilean ores to a charge consisting of

	Per Cent.
Copper	5.10
Sulphur	4.13
Iron	28.50
Manganese	7.64
Silica	23.70
Alumina	4.00
Carbonic acid	4.31
Lime	7.30
Magnesia	0.33
Phosphorus	0.05

This was charged directly into a shaft furnace 1.8 meters long, 0.9 meter wide and 0.9 meter high. The melted material

ran out into a forehearth 1.2 meters long, 0.6 meter wide and 0.6 meter high. Two carbon electrodes, 30 centimeters square by 170 centimeters long, were used in the smelting chamber, and two electrodes, 25 centimeters square by 100 centimeters long, were put in the forehearth to reheat it for tapping.

The matte obtained analyzed:

	Per Cent.
Silica	0.80
Alumina	0.50
Iron	24.30
Manganese	1.40
Sulphur	22.96
Copper	47.90

The slag contained:

Silica	27.20
Alumina	5.20
Lime	9.90
Magnesia	0.39
Iron	32.50
Manganese	8.23
Sulphur	0.57
Phosphorus	0.06
Copper	0.10

The current used was 4,750 amperes at 119 volts; power factor = 0.9; 8,000 kilograms of ore mixture were smelted in 8 hours; consumption of electrodes 50 kilograms.

Required:

(1) A balance sheet of materials entering and leaving the furnace per hour.

(2) A balance sheet of the heat development and distribution in the furnace.

(3) The saving in cost of treatment per ton of ore, assuming electrodes to cost 4 cents per kilogram, coke $20 per metric ton, and that when coke is used one-third of its calorific power leaves the furnace in the escaping hot gases. Assume all other costs similar, except that air blast costs $0.10 per ton of ore smelted additional. Electric power $6 per kilowatt-year.

(4) If the resulting slag were smelted electrically for ferro-

silicon, at an expenditure of 0.75 electric horse power-year per ton of ferro-silicon obtained, and other smelting costs were $10 per ton, how much ferro-silicon would be obtained per ton of copper ore treated, and what would be its cost?

Solution:

(1) Balance sheet per 1,000 kg. of ore.

	Charges	*Matte*	*Slag*	*Gases*
Ore: 1,000 kg.				
Silica	237 kg.	1	236	....
Alumina	40 "	0.5	39.5	....
Iron	285 "	25	260	....
Manganese	76 "	1.5	74.5	....
Sulphur	41 "	24	5	12
Copper	51 "	50	1	....
Carbonic acid	43 "	....	....	43
Lime	73 "	....	73	....
Magnesia	3 "	....	3	....
Oxygen	137 "	2	74	61
Electrode:				
Carbon	6 "	....	....	6
		104	766	122

Composition of Slag.

	Calculated.	*Analyzed.*
Silica	29.5 per cent.	27.2 per cent.
Alumina	5.0 "	5.2 "
Lime	9.2 "	9.9 "
Iron	32.5 "	32.5 "
Manganese	9.3 "	8.2 "
Sulphur	0.6 "	0.6 "

Heat Development.

Electric energy per hour:

$4{,}750 \times 119 \times 0.9 = 509$ kilowatt-hours.

$509 \times 860 = 437{,}750$ Cal. per hour.

Oxidation of carbon:

$6 \times 4{,}300 = 25{,}800$ " " "

463,550 " " "

Heat Distribution.

Heat in matte:

104×270	= 28,080	Calories.

Heat in slag:

796×400	= 318,400	"
Heat in gases	= 30,000	"
Loss by radiation and conduction	= 87,070	"
	463,550	"

The radiation and conduction loss is 19 per cent of the total heat generated in the furnace—a satisfactory showing. The useful effect of the furnace is nearly 75 per cent, reckoning as usefully applied heat that contained as sensible heat in the melted matte and slag. Nearly 90 per cent of this usefully applied heat is contained in the slag.

(3) If coke were used instead of electric heat, enough coke would have to be used to furnish 433,550 Calories plus the heat in the gases. Since the latter is assumed to be one-third of its calorific power, the coke must have a calorific power of 650,325 Calories, which at 7,000 Calories per kilogram would require 93 kg. of coke per 1,000 of ore smelted. The costs of coke and blowing engine would therefore be

Coke,	93×0.02 =	$1.96
Engine,		0.10
	Sum	$2.06

The cost of electrodes and electric energy, which would replace coke and blowing engine, would be:

Electrodes,	6 kg.×$0.04 =	$0.24
Power	509 kw.× $\frac{6.00}{8,760}$ =	0.35
	Sum,	$0.59
	Saving,	$1.47

(4) The resulting slag contains, according to the balance sheet, 260 kg. of iron, 74.5 kg. of manganese, and 236 kg. of silica equal to 126 kg. of silicon. It should produce, if com-

pletely reduced, 460 kg. of alloy (omitting the carbon it might contain) of the approximate composition:

Fe	260 kg.	= 56 per cent.
Mn	74 kg.	= 16 "
Si	126 kg.	= 28 "
	460 kg.	

Cost of power $\$6.00 \times \frac{3}{4}$	= \$4.50 per ton.
Other costs	10.00 "
Total costs per ton	\$14.50

This cost is very low, because of the very low figure assumed for power cost. However, the whole calculation points to the possibility of great saving in some localities in smelting down copper ores by electrically applied heat, and the possibility of cheaply producing, at the same spot, valuable ferrosilicon as a by-product.

CHAPTER II.

THE METALLURGY OF LEAD.

The extracting of lead from its ores and the refining of the crude metal to commercial lead, constitutes the metallurgy of lead. The chief ore is galena, lead sulphide, PbS; but the carbonate, cerussite, $PbCO^2$, and the sulphate, Anglesite, $PbSO^4$, occur at some places in important quantities; the silicate, phosphate, molybdate, tungstate, chloride and native lead are rare minerals.

The reduction of the oxidized lead ores, such as often occur at the outcrops of sulphide veins, is very simple; carbon, the cheapest and most universal reducing agent, reduces them satisfactorily at a red heat, with some loss of lead by volatilization. The sulphide of lead, however, is not reducible by carbon; it requires other treatment. If we tabulate the most common sulphides according to their thermochemical heats of formation, expressed per unit weight of sulphur held in combination (32 kilograms), we find the common metals arranged as follows:

	Calories.
Potassium (K^2, S)	103,500
Calcium (Ca, S)	94,300
Sodium (Na^2, S)	89,300
Manganese (Mn, S)	45,600
Zinc (Zn, S)	43,000
Cadmium (Cd, S)	34,400
Iron (Fe, S)	24,000
Cobalt (Co, S)	21,900
Copper (Cu^2, S)	20,300
Lead (Pb, S)	20,200
Nickel (Ni, S)	19,500
Mercury (Hg, S)	10,600
Hydrogen (H^2, S)	4,800
Silver (Ag^2, S)	3,000

A glance at this table shows us that some metals unite with sulphur more energetically than lead does, and others less energetically, and points to the theoretical possibility of decomposing lead sulphide by the agency of copper, cobalt, iron, cadmium, zinc, etc. Of these agents, iron is, of course, the cheapest and most available, and can be used to reduce lead sulphide with formation of iron sulphide.

$$\begin{array}{rrrr} PbS & + Fe & = FeS & + Pb \\ -20{,}200 & & + 24{,}000 & \end{array}$$

Showing an excess heat development per 207 parts of lead set free, of $24{,}000 - 20{,}200 = 3{,}800$ Calories. If lead sulphide and iron are brought together at a red heat, at which heat the sulphide is molten, they react energetically with evolution of heat—enough theoretically to raise the temperature of the 207 kg. of lead and 88 kg. of iron sulphide some 280° C. The reaction is fairly complete if sufficient reducing agent is present and time is allowed, so that it can be used in assaying to determine lead by fire assay, but in commercial practice more or less undecomposed lead sulphide always remains in the iron sulphide, forming a sort of double sulphide or iron-lead matte.

It is interesting to note, *en passant*, that lead vigorously reduces silver sulphide, the liberated silver alloying with the excess of lead. This reaction is accompanied by a large evolution of heat, as the table shows, is the basis of the ordinary assaying methods for silver ores, and is used commercially to extract silver from its ores wherever lead is plentiful.

The affinity of lead for oxygen is a no less interesting subject, since it concerns not only the reduction of oxide ores but also the roasting of sulphide ores to oxide, and very largely controls the refining of impurities from lead by methods involving oxidation. The heat of combination of some of the more common elements with oxygen, expressed per unit weight of 16 kilograms of oxygen held in combination, is as follows:

	Calories.
Magnesium (Mg, O)	143,400
Calcium (Ca, O)	131,500
Aluminium $\frac{1}{3}$ (Al^2, O^3)	130,870
Sodium (Na^2, O)	100,900
Silicon $\frac{1}{2}$ (Si, O^2)	98,000

	Calories.
Manganese (Mn, O)	90,900
Zinc (Zn, O)	84,800
Tin $\frac{1}{2}$(Sn, O^2)	70,650
Iron (Fe, O)	65,700
Iron $\frac{1}{3}$(Fe^2, O^3)	65,200
Nickel (Ni, O)	61,500
Hydrogen (H^2, O)	58,060
Antimony $\frac{1}{3}$(Sb^2, O^3)	55,630
Arsenic $\frac{1}{3}$(As^2, O^3)	52,130
Lead (Pb, O)	50,800
Carbon $\frac{1}{2}$(C, O^2)	48,600
Bismuth $\frac{1}{3}$(Bi^2, O^3)	46,400
Copper (Cu^2, O)	43,800
Sulphur $\frac{1}{2}$(S, O^2)	34,630
Sulphur $\frac{1}{3}$(S, O^3)	30,630
Carbon (C, O)	29,160
Mercury (Hg, O)	21,500
Silver (Ag^2, O)	7,000

Reduction of Lead Oxide.—An inspection of above table shows that lead oxide is a weak oxide, weaker than the oxides of most of the common metals. It is reduced to metallic lead by many reagents with evolution of heat. It is also reduced by some weaker reagents with absorption of heat, provided that the oxide formed is gaseous and the necessary heat energy is supplied from outside. For instance,

$$\begin{array}{ccc} PbO + C & = & Pb + CO \\ -50{,}800 & & +29{,}160 \end{array}$$

involves an absorption of 21,640 Calories, or several times as much heat as is necessary to raise the reacting substances, PbO and C, to the reacting temperature, a red heat. The reaction is endothermic, absorbing heat, and therefore only progresses *in measure as* the necessary calories are supplied from outside. The fact that all the substances concerned are liquid or solid except the product CO, gives a predisposing cause which facilitates the reaction, that is, the reaction can only go one way, since the CO gas escapes from the sphere of action as soon as formed.

Oxidation of Lead Sulphide.—When PbS is roasted, that is, heated to redness with free access of air, both the sulphur and the lead tend to oxidize, generating a large heat of oxidation, against which there is absorbed only the comparatively feeble heat of decomposition of PbS. The equation may be discussed as

$$2PbS + 3O^2 = 2PbO + 2SO^2$$
$$-(20,200) + 2(50,800) + 2(69,260)$$

The net heat evolved in the equation is $240,120 - 40,400 = 199,720$ Calories, which is 33,290 Calories per unit weight (16 kg.) of oxygen used, or 418 Calories for each kilogram of lead sulphide oxidized. This great heat of oxidation, evolved in roasting, is quite sufficient, in fact more than sufficient, to provide the heat required for self-roasting without the use of any other fuel, the chief difficulty is really to keep the charge from getting too hot and melting everything down to a liquid before the roasting is anywhere near complete. In the ordinary hand-worked reverberatory roaster, the oxidation is so slow that the fire on the grate really controls the temperature on the hearth, and the temperature of the roasting ore can be regulated accordingly. Where the roasting is done quickly, by an air blast, as in " Pot Roasting," the temperature is kept down somewhat by previously roasting off part of the sulphur, or by liberally wetting the charge, or by using limestone in with the ore, to absorb by its decomposition into CaO and CO^2 a large part of the excess heat—while the melting down of the charge is prevented by the mechanical interference presented by intermixed, inert and infusible material, such as silica, lime, etc., which simply prevents the really melted globules of sulphide from running together and thus melting down to a liquid mass.

An interesting variation is the roasting of lead sulphide to sulphate; some of this always forms, due to the high formation heat and difficult decomposability of the sulphate.

$$PbS + 2O^2 = PbSO^4$$
$$-(20,200) \quad +(215,700)$$

The net heat evolved is $215,700 - 20,200 = 195,500$ Calories, or 48,875 Calories per unit weight (16 kg.) of oxygen used, or 818 Calories for every kilogram of lead sulphide so oxidized.

This is a high heat of oxidation, and explains the great tendency to form sulphate observed during roasting. If the conditions could be found whereby only this reaction occurred, the sulphate roasting could be easily made automatic without outside fuel. There is needed, at the present time, a careful laboratory investigation of the conditions, mechanical, physical, chemical and thermal, for the roast exclusively to sulphate—just as a bit of badly needed metallurgical information.

Double Reactions.—A large part in the metallurgy of lead is played by double reactions, such as the following:

$$PbS + PbSO^4 = 2Pb + 2SO^2$$
$$PbS + 2PbO = 3Pb + SO^2$$
$$PbS + 3PbSO^4 = 4PbO + 4SO^2$$

On roasting lead sulphide for a short time, either lead or lead sulphate or mixtures of these are formed, according to the temperature and excess of air provided. With large excess of air and low temperature, and especially in presence of infusible materials which act as catalyzers (*i.e.*, which promote the union of SO^2 with O, and consequent formation of SO^3 and $PbSO^4$), sulphate may be formed almost exclusively. If the temperature is then raised, the tendency of $PbSO^4$ to react upon the undecomposed PbS rapidly gets stronger, until at an orange heat this takes place rapidly and fairly completely, forming the one single gaseous product, SO^2.

$$PbS + PbSO^4 = 2Pb + 2SO^2$$
$$-(20{,}200) - (215{,}700) + 2(69{,}260)$$

Net deficit, 97,380 Calories.

$$PbS + 2PbO = 3Pb + SO^2$$
$$-(20{,}200) - 2(50{,}800) + (69{,}260)$$

Net deficit, 52,540 Calories.

In both these cases the well-known phenomena of an endothermic reaction are manifest—the high temperature and strong firing necessary, and the formation of a single gaseous product from non-gaseous materials, assisting the reaction.

The reaction:

$$PbS + 3PbSO^4 = 4PbO + 4SO^2$$
$$-20{,}200 - 3(215{,}700) + 4(50{,}800) + 4(69{,}260)$$

Net deficit, 187,060 Calories,

is supposed to take place in " pot roasting " where excess of air is blown through the finely divided material, but it is too endothermic a reaction to take place in a pot-roasting operation to more than a very subsidiary extent.

Oxidation Refining.—Impure lead is refined or " softened " by oxidation at a red heat. We must expect a great deal of lead to be oxidized in this operation, simply because of its preponderating mass, but the impurities present will oxidize relatively faster or slower than lead in proportion as their affinity for oxygen is relatively greater or less. The skimmings or slags obtained during softening are always principally composed of lead oxide, PbO, but they come off containing, in order, zinc, tin, antimony, arsenic, bismuth and small quantities of silver. During cupellation down to silver, which is continued oxidation until all the lead is oxidized, bismuth oxide is concentrated in the last parts of lead oxide formed, which may also carry silver in small amount; before this happens, however, the lithage formed is almost chemically pure.

The converse of these oxidation reactions also holds, viz.: differential reduction. Taking a softening skimming rich in antimony, for instance, it is possible by mixing it with a small amount of reducing agent, such as carbon, to reduce out of it all the silver and considerable of the lead which it contains without reducing much antimony. This leaves the remaining unreduced material desilverized and poorer in lead, or richer in antimony, and on subsequent reduction of this by excess of reducing agent a rich antimony-lead alloy is obtained. The easy reducibility of lead oxide is complementary to the slow oxidation of lead; both facts are clear from the heat of formation of the various metallic oxides, and both are extensively utilized in the metallurgy of lead.

The Volatility of Lead.

The melting point of lead is 326°, its mean specific heat in the solid state $0.02925+0.000019t$, heat in melted lead at its melting point 11.6 Calories, latent heat of fusion 4.0 Calories, heat in just melted lead 15.6 Calories, specific heat in the liquid state 0.042—and approximately constant—boiling point at normal atmospheric pressure about 1,800° C., latent heat of vaporization, calculated by Trouton's rule (23 T) 47,680

Calories per molecular weight = 230 Calories per kilogram, assuming the vapor monatomic, specific gravity of vapor 103.5, referred to hydrogen gas at the same temperature and pressure, or, theoretically, 9.315 kg. per cubic meter at 0° C. and 760 mm. pressure, as a standard datum.

The question of the volatility of lead at other temperatures than 1,800° C. is highly important in the smelting of lead ores, yet is practically an unknown quantity. The following is an attempt to calculate these data, so important in practical metallurgy.

The vapor tension curve of mercury is known for very low and up to comparatively high pressures. A rule has been observed between mercury and water vapor, in that the absolute temperatures at which these two substances have the same vapor tensions are found to stand in the ratio 1.7 to 1 through a large range of temperatures. Since lead vapor is in all probability monatomic, like mercury vapor, we will deduce the vapor tension curve of lead from that of mercury, using the constant ratio derived from the two temperatures at which their respective vapors have atmospheric tension, viz.:

$$\frac{TPb}{THg} = \frac{1{,}800+273}{357+273} = \frac{2{,}073}{630} = 3.3$$

The following table gives the most reliable data for the vapor tension curve of mercury, and the corresponding data calculated for lead, assuming the constant ratio 3.3 between the absolute temperatures at which they have the same vapor tension:

Tension of Vapor *mm. of Hg.*	*Mercury* *C°*	*Lead* *C°*
0.0002	0	625
0.004	33	735
0.045	67	844
0.28	100	954
1.47	133	1,064
5.73	167	1,173
18.25	200	1,283
50.	233	1,393
106.	267	1,502

Tension of Vapor		*Mercury*	*Lead*
mm. of Hg.		*C°*	*C°*
242.		300	1,612
484.	*Atmospheres.*	333	1,722
760.	= 1.0	**357**	**1,800**
849.	= 1.1	367	1,841
1588.	= 2.1	400	1,951
	4.3	450	2,116
	8.0	500	2,280
	13.8	550	2,445
	22.3	600	2,609
	34.	650	2,774
	50.	700	2,938
	72.	750	3,103
	102.	800	3,267
	137.5	850	3,436
	162.	880	3,525

From the above table a vapor pressure curve of mercury and lead can be constructed. An examination of the data shows that lead is certainly volatile to a minute extent at a low red heat, and that a current of inert gas passing across the surface of melted lead at that temperature certainly carries away vapor of lead; at the melting point of silver the tension is only about one-quarter of a millimeter, or one three thousandth of an atmosphere, yet this means that each cubic meter of inert gas carries off one three-thousandth of its volume, or one-thirtieth of 1 per cent of its volume, of lead vapor. At 1,300°, the temperature of a commercial zinc retort, or of a lead smelting furnace, the tension is about one-fortieth of an atmosphere, which would mean that any other gas or vapor could carry 2.5 per cent of its volume of lead vapor with it. It must be remembered, moreover, that such gas saturated with lead vapor if suddenly cooled does not deposit its excess of lead vapor as liquid lead, but that a suspension similar to hoarfrost almost inevitably results, the so-called "lead fume," which is simply molecularly divided liquid or solid lead carried in suspension by a current of gas. The lead vapor is thus almost entirely carried out of the furnace without condensation and deposition.

Looking at the higher pressures, we can understand why an

explosive reaction results when PbO is reduced by finely divided aluminium, the " aluminothermic " reaction. The immense heat liberated in the reaction,

$$3PbO + 2Al = 3Pb + Al^2O^3,$$

220,000 Calories, raises the products to an electric furnace temperature, to some 3,000° C., at which temperature the lead vapor has a maximum tension, according to our table, of 60 atmospheres. No wonder, then, that when Tissier tried this test for the first time, in 1857, using a piece of sheet aluminium weighing less than 3 grams (0.1 ounce), " le creuset a été brisé en mille pieces et les portes du fourneau projetées au loin "—the crucible was broken into a thousand pieces and the doors of the furnace blown to a distance.

Roasting of Lead Ores.

The principal operations in the metallurgy of lead are the roasting of the ore, its reduction to metal and the refining of the crude metal.

The chief ore of lead being galena, PbS, the operation of roasting it in air converts it partly into PbO and partly into $PbSO^4$. Since PbS is easily fusible, and is volatile *per se* at a yellow heat, it is necessary to roast carefully and slowly, avoiding high temperatures, which first make the ore sticky or pasty and afterwards fuse it, thus practically stopping the roasting reaction. The only manner in which rapid roasting can be done is by having the ore mixed with so much infusible inert matter, like lime, that the globules of melted sulphide cannot run together, but are kept isolated and continue to oxidize on their surfaces, the mass being meanwhile kept " open " or porous by the inert, infusible material, to allow the rapid passage of air through the mass. This is the principle of " pot roasting "—the most radical improvement of recent years in the metallurgy of lead.

Problem 123.

A Savelsberg " pot roaster " treats 5 tons of ore mixture, consisting of 100 parts lead ore, 10 parts quartzose silver ore, 10 parts spathic iron ore, 19 parts limestone. The lead ore is galena ore, containing 78 per cent of lead and 15 per cent of

sulphur; the silver ore may be called silica sand; the spathic iron ore $FeCO^3$; the limestone $CaCO^3$. The mixture is moistened with 5 per cent of its weight of water. Air blast is kept constant at 7 cubic meters per minute, blower displacement at 15° C., and the operation lasts 18 hours, leaving 2 per cent of sulphur in the product, which may be assumed as undecomposed PbS. Gases produced contain approximately 10 per cent of SO^2 and 5 per cent free oxygen; 50 kg. of charcoal is used to start the operation, and is assumed to be pure carbon.

Required:

(1) The weight of product and its percentage composition.

(2) The complete analysis of the gases escaping.

(3) The efficiency of delivery of the blower.

(4) The proportion of the heat generated by the oxidation of the ore which is absorbed in the decomposition of the limestone.

(5) The proportion of the heat generated in the pot used in evaporating the moisture of the charge.

(6) The proportion of the heat generated in the pot carried away by the gases at an average temperature of 300° C.

(7) Make a heat balance sheet of the whole operation.

Solution:

(1) The components of the 5-ton (=5,000 kilos) charge are:

Galena	3597 kg.	= Pb	2806 kg.	S:	540 kg.		
Silver ore	360 "	= SiO^2:	360 "				
Iron ore	360 "	= FeO:	224 "	CO^2:	136 "		
Limestone	683 "	= CaO:	382 "	CO^2:	301 "		

Approximate composition of product:

PbO	$2806 \times \frac{223}{207}$	= 3023 kg.
SiO^2		= 360 "
FeO		= 224 "
CaO		= 382 "
		3989 "

But, since product contains 2 per cent of sulphur as undecomposed PbS, the above weight is only 99 per cent of the

weight of the roasted ore, because the lead combined with this sulphur has been calculated above to PbO, and the O in PbO is only half the weight of the S in PbS. The above weight is short, therefore, by an amount equal to one-half the weight of the sulphur present, and since the latter is 2 per cent of the roasted ore the above weight is 1 per cent short. The corrected weight of the roasted ore is, therefore,

$$3{,}989 \div 0.99 = 4{,}029 \text{ kg.},$$

and its sulphur content 81 kg., corresponding to 521 kg. of lead, or 602 kg. of PbS. This leaves present, as PbO, 2,806 − 521 = 2,285 kg. of lead, equal to $2{,}285 \times 223/207 = 2{,}461$ kg. of PbO.

Revised composition of product:

PbO	2461 kg.	= 61	per cent
PbS	602 "	= 15	"
SiO^2	360 "	= 9	"
FeO	224 "	= 5	"
CaO	382 "	= 9	"
	4029 "		(1)

(2) The charge gives to the gases

H^2O	$5000 \times 0.05 = 250$ kg.
CO^2	$(50 \times 3.67) + 136 + 301 = 620$ "
S	$540 - 81 = 459$ "

and the blast gives to the charge

$$O\ 2461 - 2285 = 176 \text{ kg.}$$

The volume of SO^2 produced from 459 kg. of sulphur, which makes 918 kg. of SO^2, will be, at standard conditions,

$$918 \div \left(0.09 \times \frac{64}{2}\right) = 319 \text{ cubic meters.}$$

The free oxygen in the gases is half the volume of the SO^2, and, therefore, will be exactly one-quarter of its weight.

The volumes of H^2O and CO^2 present in the gases, at standard conditions, are

H^2O $250 \div \left(0.09 \times \frac{18}{2}\right) = 309$ cubic meters.

CO^2 $620 \div \left(0.09 \times \frac{44}{2}\right) = 313$ " "

The nitrogen present is that in the air used, or 10/3 the weight of oxygen in the air. The latter is the weight of oxygen in the PbO of the roasted charge, plus the oxygen necessary to burn the 50 kg. of charcoal, plus the oxygen oxidizing sulphur to SO^2 and the free oxygen in the gases.

O in PbO		=	176 kg.
O to burn C	$50 \times \frac{32}{12}$	=	133 "
O to burn S	$459 \times \frac{32}{32}$	=	459 "
Free O^2 in the gases		=	230 "
	Total		998 "
N^2 corresponding		=	3327 "

Composition of escaping gases:

				Per Cent.
Nitrogen	3327 kg.	= 2609	cu. meters	= 70.3
Oxygen	230 "	= 159	" "	= 4.3
SO^2	918 "	= 319	" "	= 8.6
CO^2	620 "	= 313	" "	= 8.5
H^2O vapor	250 "	= 309	" "	= 8.4
		3709		100.

(2)

(3) Oxygen delivered by blast 998 kg.
Nitrogen in the blast 3327 "
Air delivered 4325 "

Volume at $0° = 4325 \div 1.293 = 3345$ cu. meters.

Volume at $15° = 3345 \times \frac{288}{273} = 3529$ " "

Displacement of blower at 15°

$$7 \times 60 \times 18 = 7560 \text{ “ “}$$

Efficiency of blower $\frac{3529}{7560} = 0.467 = 46.7$ per cent. (3)

(4) The heat generated in the oxidation of the ore consists of the heat of formation of the PbO formed, plus that of the SO^2, and less that of the PbS decomposed. This is not the complete heat balance of the whole operation, but simply that concerned with the oxidation of the galena.

Heat of oxidation of Pb to PbO

2285 kg. Pb. $\times 245$ = + 559,825 Cal.

Heat of oxidation of S to SO^2

459 kg. S $\times 2164$ = + 993,275 “

Heat of formation of PbS decomposed

2285 kg. Pb $\times 98$ = − 223,930 “

Roasting heat = +1,329,170 “

The decomposition of the limestone, producing 301 kg. of CO^2, absorbs

$$301 \times 1{,}026 = 308{,}825 \text{ Cal.}$$

The proportion of the roasting heat thus absorbed is

$$\frac{308{,}825}{1{,}329{,}170} = 0.232 = \mathbf{23.2} \text{ per cent.} \quad (4)$$

(5) The 5-ton charge is moistened with 5 per cent of its weight of water, or 250 kgs., in order to keep down the temperature. This absorbs, simply in becoming vapor,

$$250 \times 606.5 = 151{,}625 \text{ Cal.},$$

Which, on the heat generated in the roasting operation, is

$$\frac{151{,}625}{1{,}329{,}170} = 0.114 = \mathbf{11.4} \text{ per cent.} \quad (5)$$

(6) If the gases pass away at an average temperature of 300°, and the air comes in at an average temperature of 15°, the

gases cool off the pot to the extent of the difference between these two heat capacities:

Heat in the air entering:

$$3345\ m^3 \times [0.303 + 0.000027(15)] \times 15 = 15{,}225\ \text{Cal.}$$

Heat in gases escaping:

N^2 2609 m^3 / O^2 159 m^3	$\times[0.303+0.000027(300)]$	=	861.1 Cal. per 1°.
SO^2 319 m^3	$\times[0.36+0.0003(300)]$	=	143.6 "
CO^2 313 m^3	$\times[0.37+0.00022(300)]$	=	136.5 "
H^2O 309 m^3	$\times[0.34+0.00015(300)]$	=	119.0 "
			1260.2 "

$$\text{Total} = 1260.2 \times 300 = 378{,}060\ \text{Cal.}$$

Proportion of the total roasting heat thus carried out:

$$\frac{362{,}835}{1{,}329{,}070} = 0.280 = \mathbf{28.0}\ \text{per cent.} \qquad (6)$$

(7) *Heat Available.*	*Calories.*
Sensible heat of air blast, at 15°	15,225
Combustion of charcoal	405,000
Net heat generated by the roasting	1,329,170
Total	1,749,395

Heat Distribution.

Sensible heat in the hot gases	378,060 = 22	per cent.
Decomposition of carbonates:		
Calcium carbonate	308,825 = 18	"
Iron carbonate	76,980 = 4	"
Evaporation of moisture	151,625 = 9	"
Sensible heat of product, at 400°	400,000 = 23	"
Loss by radiation and conduction	433,905 = 25	"
	1,749,395	

Reduction of Roasted Ore.

If the roasted ore is reduced in reverberatory furnaces, the chances are that the undecomposed sulphide it contains will react with the oxide or sulphate, forming metal and SO^2, and

thus eliminating almost all of the sulphur left in the roasted ore; this results in the formation of no matte, or at most of very little rich matte. If the roasted ore is reduced in shaft furnaces, the carbonaceous fuel and strong reducing atmosphere of the same, tend to reduce oxides to metal and sulphates to sulphides before they reach the temperature at which they can react on sulphide, thus cutting out very largely the double reaction, and throwing into matte the larger part of the sulphur left in the roasted ore. This is highly advantageous if the ore has copper in it, even if only in small amount, as the matte will concentrate the copper in it, is easily separated from the metal and the slag, and forms a valuable by-product. Since most lead ores contain some copper, enough to make it pay to save it, the roasting of these is never pushed to completion, and the reduction in low shaft furnaces, run at moderate temperature, is pursued with the object of producing a copper-iron matte. Any arsenic or antimony left in the roasted ore is likely also to form *spiess*, a compound of arsenic and antimony with iron, copper, nickel, cobalt, lead and silver, which is heavier than matte, but lighter than lead, and separates out in the cooling pots between these. It is a highly undesirable product, because of its complexity and the difficulty of satisfactorily and cheaply separating its constituents; it is always to be advised to remove arsenic and antimony as completely as possible in the roasting operation, even at the expense of removing too much sulphur, and then to supply the sulphur needed in the smelting operation by mixing with the dead-roasted ore some raw sulphide ore free from arsenic and antimony, if such can be obtained.

In calculating the charge for such a smelting operation, the roasted ore must be charged with such amounts of iron ore and limestone as will, together with the gangue of the ore and the ash of the fuel used, make an easily fusible slag. To produce such a slag is of fundamental importance, since it must melt and become thinly liquid at the moderate temperature necessarily prevailing in a lead furnace. Experience has shown that a typical lead slag will contain about 30 per cent SiO^2, 40 per cent FeO and 20 per cent CaO, with 10 per cent allowed for other ingredients, such as Al^2O^3, etc., or in more general terms, that SiO^2, FeO and CaO are best present in the propor-

tions 30 : 40 : 20. The other limitations are that a certain amount of hand-picked slag is always returned to the furnace for re-smelting and purification from matte, and that the fuel, coke, cannot melt more than a certain amount, say seven times its weight of inert material. With these conditions in mind, we will work out a typical smelting problem, the data for which are taken from Hofman's *Metallurgy of Lead.*

Problem 124.

A mixture of lead carbonate ore and galena (which represents pretty closely a partially roasted sulphide ore) is smelted with the addition of iron ore and limestone. The charges for the furnace consist of 1,000 pounds of burden (material to be smelted) and 150 pounds of coke (containing 10 per cent ash), and the 1,000 pounds consist of 100 pounds return slags and 900 pounds of lead ore, iron ore and limestone. The percentage composition of these materials is:

	Lead Ore.	*Iron Ore.*	*Limestone.*	*Ash of Coke.*
SiO^2	32.6	4.3	2.7	40.3
FeO	14.8	72.4	4.5	26.5
MnO	4.3	1.7	...	....
CaO	2.2	3.1	37.3	6.9
MgO	5.3	....	11.9	2.4
Al^2O^3	2.5	....	....	20.4
BaO	1.5			
ZnO	2.4			
S	4.4			
As	0.5			
Pb	20.7			
Cu	2.9			
Ag	0.17			

The iron present in these materials is really present mostly as Fe^2O^3 and only partly as FeO, but the analysis is expressed usually as FeO in order to facilitate the slag calculations. The analyses, as given, are not expected to add up to 100.

In making the calculations, assume that the slag to be produced contains SiO^2: FeO: CaO in the ratio 30 : 40 : 20; that the FeO here expressed includes the MnO, calculated to its FeO equivalent, and the CaO includes the MgO, BaO, and ZnO calculated to their CaO equivalent. Assume also that all the ZnO of the charge goes into the slag, all the sulphur into matte, all the arsenic into speiss, of the formula Fe^5As, all the silver and lead into the lead bullion.

Requirements:

(1) The proportions of lead ore, iron ore and limestone to be used in the 900 pounds of these to a charge.

(2) The weight and composition of the slag formed.

(3) The weight and composition of matte formed.

(4) The weight and composition of speiss formed.

(5) The weight and composition of lead bullion formed.

(6) A balance sheet of the essential materials entering and leaving the furnace.

Solution:

(1) There are really only two unknown weights to be determined, for the sum of the three weights required is to be 900. Similarly, the ratio 30 : 40 : 20 really gives two conditions to be fulfilled, since there are practically two ratios to be worked to. The simplest method of solution is, undoubtedly, the algebraic one, letting x and y represent two of the ores, $900-(x+y)$ the other, and then working out the weights of SiO^2, FeO and CaO in the slag, expressed in terms of x and y. The ratio 30 : 40 : 20 then gives us two independent equations, containing the two unknowns, and the problem is solved.

Let x = weight of lead ore.
y = weight of iron ore.
$900-x-y$ = weight of limestone.
15 = weight of ash of coke.
100 = weight of return slags.

Calculation of FeO going into Slag.

Sulphur in 100 parts ore		4.4 lbs.
Copper in 100 parts ore		2.9 "
Sulphur united with Cu to form Cu^2S		0.7 "
Sulphur left over to form FeS		3.7 "
Iron needed to form FeS $= 3.7\times\frac{56}{32}$	=	6.5 "
FeO corresponding to this Fe $= 6.5\times\frac{72}{56}$	=	8.4 "
Arsenic in 100 parts of ore		0.5 "
Iron required to form $Fe^5As = 0.5\times\frac{280}{75}$	=	1.9 "

FeO corresponding to this Fe $= 1.9 \times \frac{72}{56}$ $= 2.4$ lbs.

Total FeO disappearing in matte and speiss $= 10.8$ "
FeO left over to go into slag $= 14.8 - 10.8$ $= 4.0$ "

Therefore x parts of lead ore contributes to the slag:

SiO^2.....0.326 x
FeO.....0.040 x
MnO.....0.043 x = 0.044 x FeO.
CaO.....0.022 x
MgO.....0.053 x = 0.074 x CaO.
Al^2O^3.....0.025 x
BaO.....0.015 x = 0.006 x CaO.
ZnO.....0.024 x = 0.017 x CaO.

The FeO equivalent of MnO is 72/71 the MnO; the CaO equivalent of MgO is 56/40 the MgO, of BaO is 56/141 the BaO, of ZnO is 56/81 the ZnO. These ratios are the chemically equivalent values of these oxides, as taken from their molecular weights. Adding all these together, our lead ore contributes to the slag the equivalent of

SiO^2 0.326 x, FeO 0.084 x, CaO 0.119 x.

The y parts of iron ore similarly contributes to the slag:

SiO^2 0.043 y, FeO 0.741 y, CaO 0.031 y.

The $900 - x - y$ parts of limestone contributes likewise:

SiO^2 $0.027(900 - x - y)$
FeO $0.045(900 - x - y)$
CaO $0.373(900 - x - y)$
MgO $0.119(900 - x - y) = 0.167(900 - x - y)$ of CaO.

Therefore, total contribution of the limestone to the slag:

SiO^2 $0.027(900 - x - y)$, FeO $0.045(900 - x - y)$,
CaO $0.540(900 - x - y)$.

Contribution of ash of fuel to the slag, in similar manner:

SiO^2 6.1 FeO 4.0 CaO 1.4

Adding all these together, we have in the slag:

SiO^2 ..... $30.4+0.299\,x+0.016\,y$
FeO ..... $44.5+0.039\,x+0.696\,y$
CaO ..... $487.6-0.421\,x-0.509\,y$

According to assumption, these ingredients as thus summated should bear the relations 30 : 40 : 20. We therefore have

$$30.4+0.299\,x+0.016\,y = \frac{30}{20}(487.6-0.421\,x-0.509\,y)$$

$$44.5+0.039\,x+0.696\,y = \frac{40}{20}(487.6-0.421\,x-0.509\,y)$$

Whence
x = lead ore = **523** lbs.
y = iron ore = **274** "
$900-x-y$ = limestone = **103** " (1)

(2) With the weights of materials used, as calculated, we can calculate the weights of the ingredients of the slag as:

	Lead Ore.	*Iron Ore.*	*Limestone.*	*Coke Ash.*	*Total.*
SiO^2	170.5	11.8	2.8	6.1	191.2
FeO	20.9	198.4	4.6	4.0	227.9
MnO	22.5	4.7	....	....	27.2
CaO	11.5	8.5	38.4	1.0	59.4
MgO	27.7	....	12.3	0.4	40.4
Al^2O^3	13.1	....	....	3.1	16.2
BaO	7.8	....	....	....	7.8
ZnO	12.6	....	....	....	12.6
					582.7

Percentage Composition and Check on Ratio.

SiO^2 ..... 32.8 per cent
FeO ..... 39.0 "
MnO ..... 4.7 " = 4.8 per cent FeO.
CaO ..... 10.2 "
MgO ..... 6.9 " = 9.7 " CaO.
Al^2O^3 ..... 2.8 "
BaO ..... 1.3 " = 0.5 " CaO.
ZnO ..... 2.2 " = 1.5 " CaO.

Summated SiO^2 : FeO : CaO
= 32.8 : 43.8 : 21.9 = 30 : 40 : 20

(3) Sulphur in 523 lbs. of lead ore = 23.0 lbs.
Copper in 523 lbs. of lead ore = 15.2 "
Sulphur to form Cu^2S with this Cu = 3.8 "
Sulphur to form FeS = 23.0 − 3.8 = 19.2 "

Fe to form FeS = $19.2 \times \frac{56}{32}$ = 33.6 "

FeS in matte = 19.2 + 33.6 = 52.8 "
Cu^2S in matte = 15.2 + 3.8 = 19.0 "

Total weight of matte = **71.8** "
(3)

Composition of matte

Cu^2S	= 26.5 per cent =	Cu	= **21**	per cent.
FeS	= 73.5 "	Fe	= **47**	"
		S	= **22**	" (3)

(4) Arsenic in 523 lbs. of lead ore = 2.6 "

Fe to form Fe^5As = $2.6 \times \frac{280}{75}$ = 9.7 "

Weight of speiss formed = **12.3** "
(4)

Composition: Fe **79** per cent
As **21** " (4)

(5) Lead in 523 lbs. of lead ore = 108.3 lbs.
Silver in 523 lbs. of lead ore = 0.9 "

109.2 "
(5)

Composition: Pb **99.2** per cent.
Ag **0.8** " (5)

(6) Balance sheet of materials entering and leaving per 1,000 lbs. of burden:

Charges.		*Bullion.*	*Matte.*	*Speiss.*	*Slag.*	*Gases.*
Lead Ore 523						
SiO^2	170.5	...	....	...	170.5	....
FeO	77.4	...	Fe 33.6	Fe 9.7	Fe O20.9	O 13.2
MnO	22.5	...	....	...	22.5	....
CaO	11.5	...	....	...	11.5	....

Charges.		*Bullion.*	*Matte.*	*Speiss.*	*Slag.*	*Gases.*
MgO	27.7	...	....	...	27.7	....
Al^2O^3	13.1	...	....	...	13.1	....
BaO	7.8	...	....	...	7.8	....
ZnO	12.6	...	....	...	12.6	....
S	23.0	...	23.0	...	....	....
As	2.6	...	....	2.6	....	....
Pb	108.3	108.3	....	...	....	....
Cu	15.2	...	15.2	...	....	....
Ag	0.9	0.9	....	...	....	....
Iron Ore	**274**					
SiO^2	11.8	...	....	...	11.8	....
FeO	198.4	...	....	...	198.4	....
MnO	4.7	...	....	...	4.7	....
CaO	8.5	...	....	...	8.5	....
Limestone	**103**					
SiO^2	2.8	...	....	...	2.8	....
FeO	4.6	...	....	...	4.6	....
CaO	38.4	...	....	...	38.4	....
MgO	12.3	...	....	...	12.3	....
Ash of Fuel	**15**					
SiO^2	6.1	...	....	...	6.1	....
FeO	4.0	...	....	...	4.0	....
CaO	1.0	...	....	...	1.0	....
MgO	0.4	...	....	...	0.4	....
Al^2O^3	3.1	...	....	...	3.1	....
Return Slag	**100**	...	....	...	100.0	....
		109.2	71.8	12.3	682.7	13.2

THE ELECTROMETALLURGY OF LEAD.

As far as the present, the use of electrical methods in the metallurgy of lead has been confined to the Salom process of cathodic reduction of galena and the Betts process of refining crude lead bullion. Electrothermic methods of smelting, and even of roasting, are among future possibilities, as are also the leaching by suitable solvents and electrical precipitation of lead from the solutions, but they have not been commercially practiced.

The Salom process puts the powdered galena on a "hard-

lead " plate, in a solution of dilute sulphuric acid, and using a " hard-lead " anode, passes a strong current through, reducing PbS *in situ* to Pb with formation of H^2S (with some hydrogen) at the cathode and oxygen at the anode. It was run commercially on a fair scale at Niagara Falls. For further details reference may be made to *Transactions American Electrochemical Society*, Vol. I, p. 87; II, p. 65; IV, p. 101.

The Betts process consists in using impure lead as anode in a solution of lead fluo-silicate, PbF^2. SiF^4, strongly acid with HF. The refining plant and its operation are quite similar to a copper refining plant. The cathodes are sheet steel, greased, and the dense sheet lead deposited is stripped off from time to time.

Problem 125.

In a Salom apparatus powdered galena, density of powder 3.5, is placed in a layer 0.5 mm. thick on a revolving lead table having an effective treatment area of 2.25 square meters. Current density 330 amps. per square meter of cathode surface. Time of treatment of the layer 90 minutes. Electrolyte dilute H^2SO^4. Resistance of cell 0.001 ohm. Heats of formation: (Pb, S) 20,300; (H^2, S) 4,800 (as gas); (H^2, O) 69,000. Assume reduction to Pb complete.

Required:

(1) The efficiency of application of the amperes passing to the reduction of the galena, and the percentage of ampere efficiency lost by the evolution of hydrogen.

(2) The average composition of the gases coming from the cell and their volume per hour, at normal pressure and 20° C., assuming the electrolyte saturated with H^2S, H^2 and O^2 at starting.

(3) The working voltage absorbed, if the efficiency of reduction of galena were 100 per cent.

(4) The working voltage if the cell were kept running after all the galena was reduced.

(5) The average working voltage of the cell in actual operation and the distribution of this.

(6) The proportion of the power required by the cell which could be generated by burning the gases produced in a gas engine (if such were possible) at a thermo-mechanical efficiency of 100 per cent.

(1) Current used 2.25×330 = 742 amperes.

Lead theoretically reducible in 90 minutes

$0.00001035 \times 103.5 \times 60 \times 90 \times 742.5$ = 4295 grams.

Galena in the apparatus:

$2.25 \times 10{,}000 \times 0.05 \times 3.5$ = 3938 "

Lead under treatment:

$$3938 \times \frac{207}{239} = 3410 \text{ "}$$

Ampere efficiency of the treatment:

$$\frac{3410}{4295} = 0.794 = \mathbf{79.4} \text{ per cent.}$$

Per cent of amperes evolving hydrogen = **20.6** " (1)

(2) If all the current evolved H^2S, the gases evolved would be:

$2H^2S$ O^2

2 parts 1 part.

If all the current evolved H^2, the gases would be:

$2H^2$ O^2

2 parts 1 part.

If 79.4 per cent of the current evolves H^2S and 20.6 per cent hydrogen, the average gases evolved will be:

H^2S	1.588 parts	=	**52.93** per cent.
H^2	0.412 "	=	**13.73** "
O^2	1.000 "	=	**33.33** " (2)

The volume evolved per hour is found as follows:

Oxygen produced by 1 ampere hour

$0.00001035 \times 8 \times 60 \times 60$ = 0.29808 grams.

Produced by 742.5 amperes, in one hour

0.29808×742.5 = 221.3 "

Volume at 760 mm. and 0° C.

$221.3 \div 1.44$ = 153.7 litres.

Volume of gases produced per hour

153.7×3 = 461. "

= 0.461 cubic meter

Volume at 20°

$$0.461 \times \frac{273+20}{273} = \mathbf{0.495} \text{ " (2)}$$

(3) Voltage for ohmic resistance

$$0.001 \times 742 = 0.742 \text{ volts.}$$

Chemical work done if only H^2S is formed, per formula

$$PbS + H^2O = H^2S + O + Pb$$

$$-20{,}300 \qquad -69{,}000 \qquad +4{,}800 = -84{,}500 \text{ Cal.}$$

Per chemical equivalent concerned $= -42{,}250$ "

Voltage absorbed in chemical work

$$42{,}250 \div 23{,}040 = 1.83 \text{ volts}$$

Total voltage drop in the cell $1.83 + 0.74 =$ **2.59** " (3)

(4) Chemical work done if only H^2 is liberated = 69,000 Cal.

Voltage absorbed in chemical work

$$\frac{69{,}000}{2} \div 23{,}040 = 1.49 \text{ volts.}$$

Total voltage drop in the cell = **2.23** (4)

(5) Voltage absorbed in chemical work if 79.4 per cent of the current evolves H^2S and 20.6 per cent H^2:

$$(1.83 \times 0.794) + (1.49 \times 0.206) = 1.76 \text{ volts.}$$

Total voltage drop, in average running = **2.50** " (5)

Logically, the 1.76 volts absorbed in chemical decomposition in average running is properly calculated thus, from the energy evolved:

$$\frac{(42{,}250 \times 0.794) + (34{,}500 \times 0.206)}{23{,}040} = 1.76$$

(6) Heat of combustion of 1 cubic meter of the average gas:

H^2S	$0.5293 \text{ m}^3 \times 5{,}513$	= 2918 Cal.
H^2	$0.1373 \text{ m}^3 \times 2{,}614$	= 359 "
	Sum	= **3277** "

Calorific power of gas produced per hour:

$$3277 \times 0.461 = 1511 \text{ Calories.}$$

Watt hours producible from this at 100 per cent thermo-mechanical efficiency:

$$1511 \div 0.860 = 1757 \text{ watts.}$$

Current used by the cell, average running:

$$742.5 \times 2.50 = 1856 \text{ watts.}$$

Proportion theoretically regainable:

$$\frac{1757}{1856} = 0.95 = \mathbf{95} \text{ per cent.} \qquad (6)$$

The reason why more power is theoretically regainable than is used in doing chemical work in the cell, is that the gas engine burns the sulphur of the PbS ultimately to SO^2, and this is the source of great energy, while only a relatively small amount of energy was necessary to convert the PbS into H^2S ready for combustion.

Problem 126.

Lead bullion refined by the Betts process is 96.73 per cent lead, and the refined lead is practically pure. The anodes are 1.5 inches thick, and weigh, with lugs for suspension, 275 pounds. They are left in the tanks an average of nine days, running with 135 amps. per plate, whose active surface is 1,700 square inches. Space between anode and cathode $1\frac{1}{8}$ inches, specific resistance of solution 10 ohms. Each tank has twenty-two anodes and twenty-three cathodes, and produces an average of 545 pounds of lead per day. Power costs $50 per electric horsepower-year, as delivered to the tanks. Drop per tank, due to resistance of contacts, 0.15 volt; specific gravity of pure lead, 11.35.

Required:

(1) The weight of lead theoretically deposited by the current per day.

(2) The ampere efficiency of the deposition.

(3) The voltage drop per tank.

(4) The amount of anode scrap to be remelted in percent of the total anode weight.

(5) The average thickness of the cathode deposit per day.

(6) The power costs per ton of impure lead refined.

Solution:

(1) Lead theoretically deposited by 1 ampere per day

$$0.00001035 \times 103.5 \times 60 \times 60 \times 24 = 92.55 \text{ grams.}$$

Per anode per day, dissolved

$$92.55 \times 135 \div 1000 = 12.5 \text{ kg.}$$
$$= 27.5 \text{ lbs.}$$

Per tank, per day, deposited

$$27.5 \times 22 = \mathbf{605} \text{ "} \qquad (1)$$

(2) Efficiency of deposition

$$\frac{545}{605} = 0.90 = \mathbf{90} \text{ per cent.} \qquad (2)$$

(3) Amperes used per plate = 135

Current density per square inch

$$= 135 \div 1700 = 0.0794 \text{ amperes}$$

Current density per square centimeter

$$= 0.0794 \div 6.25 = 0.0127 \text{ "}$$

Distance of plates apart = 1.17 inches
= 2.93 cm.

Resistance of 1 cm. cube of electrolyte = 10 ohms.

Voltage drop in electrolyte

$$10 \times 2.93 \times 0.0127 = 0.37 \text{ volt.}$$

Voltage drop in connections = 0.15 "
Total voltage drop per tank = **0.52** " **(3)**

(4) Dissolved from anode in 9 days

$$545 \div 22 \times 9 = 223 \text{ lbs.}$$

Anode corroded in 9 days, assuming slime to fall off it

$$223 \div 0.9673 = 231 \text{ lbs.}$$

Anode scrap = 275 − 231 = 44 "

Percentage of anode scrap $\frac{44}{275} = 0.16 =$ **16** per cent. (4)

(5) Deposit of lead one side of a cathode, per day

$$545 \div 44 = 12.4 \text{ lbs.}$$
$$= 5.636 \text{ kg.}$$

Area of 1 side of a cathode = 850 sq. inches.
= 5312 sq. cm.

Deposit, per day, per sq. cm.

$$5636 \div 5312 = 1.06 \text{ grams.}$$

Volume of this deposit $1.06 \div 11.35 =$ 0.093 cu. cm.

Therefore thickness deposited per day = **0.93** mm. (5)

(6) Bullion refined, per tank, per day
$545 \div 0.9673 =$ 563 lbs.

Power required per tank $2970 \times 0.52 =$ 1544 watts.
$=$ 2.06 e.h.p.

Cost of power per year $= 50 \times 2.06 =$ 103. dollars.

per day $= 103 \div 365 =$ 0.28 "

per ton of lead treated $0.28 \times \frac{2000}{563} =$ **0.99** " (6)

CHAPTER III.

THE METALLURGY OF SILVER AND GOLD.

The processes most used for the extraction of silver and gold from their ores are the smelting of the ores with copper ores to matte and eventually blister copper, followed by electrolytic refining of the latter, or smelting with lead ores, followed by desilverization of the resulting lead bullion, cupellation of the rich lead, or electrolytic refining of the same. In all of these cases the silver or gold is a comparatively minute constitutent of the ore, intermediate products and final metal, so that the metallurgy of silver or gold, after these methods, up to the production of impure silver or gold, or silver or gold bullion, is practically the metallurgy of copper or lead—both of which subjects we have considered at length.

When we obtain products in which the silver or gold is the chief constituent, we approach a condition in which calculations upon the precious metal contained may be based, but here again there are not the same conditions of economy so prominent in the metallurgy of lead or copper. It does not matter greatly, for instance, whether we use 50 cents' worth of one fuel or a dollar's worth of another in melting 1,000 ounces of silver worth over $500; the question of which fuel is the cleanest or most convenient is of greater importance than the cost of the fuel.

The object of this introduction is to show that, until it comes to handling nearly pure silver or gold, close calculations as to amounts of reagents, running of furnaces, etc., are not practicable for silver or gold, *per se*.

Electrolytic Refining of Silver Bullion.

The parting of gold and silver by acids is rapidly giving place to the cleaner and less expensive electrolytic separation. The bullion may be of quite variable composition. The following analyses of two samples give an idea of this variation.

	Cupelled Silver.	*Impure Silver.*
Ag	98.69	74.08
Pb	1.09	3.71
Cu	0.12	20.23
Fe	0.09	1.01
Au	0.0023	0.05

The electrolytic refining proceeds easiest with the nearly pure silver, because the impurities going into solution accumulate much more slowly, and the solution therefore requires purifying less frequently. On the other hand, the solution of a large amount of copper, iron or lead adds electromotive force to the circuit, since silver only is deposited, and thus decreases the electrical work to be done.

Problem 127.

Two varieties of silver bullion are refined electrolytically carrying

	No. 1.	*No.* 2.
Ag	98.69	74.08
Pb	1.09	3.71
Cu	0.12	20.23
Fe	0.09	1.01
Au	0.01	0.05

The slimes from each carry in percentages:

	No. 1.	*No.* 2.
Ag	60	55
Pb	10	5
Cu	5	15
Fe	3	5
Au	22	20

In each case all the gold goes into the slimes. A current density of 200 amperes per square meter of electrode surface is used, and the plates are 2 centimeters thick. Specific gravity of No. 1, 10.15; of No. 2, 9.79. There is anode scrap equal to 12 per cent of the weight of the plates. The working space between the electrodes is 4 cm. total current 220 amperes per tank, specific resistance of electrolyte 20 ohms. Deposited silver, 19.85 kg. per tank per day.

Required:

(1) The ampere efficiency of the deposition of silver.

(2) The weight of anode corroded in a tank per day.

(3) The deficit in weight of silver in the electrolyte in each tank per day.

(4) The electromotive force contributed to the circuit by the solution of impurities in the case of each bullion.

(5) The total drop of potential across each tank, adding 10 per cent for loss in contacts.

(6) The horse power-hours required per kilogram of silver deposited in each case.

Solution:

(1) Silver deposited theoretically by one ampere, per day

$$0.00001035 \times 108 \times 60 \times 60 \times 24 = 96.58 \text{ grms.}$$

220 amperes deposit $96.58 \times 220 = 21{,}248$ "

$= 21.248$ kg.

$$\text{Ampere efficiency } \frac{19.85}{21.248} = 0.934 = \mathbf{93.4} \text{ per cent.} \qquad (1)$$

This means that 6.6 per cent of all the silver which the current is capable of depositing is prevented from depositing by the nitric acid present, forming $AgNO^3$. The electrolyte is silver nitrate with copper nitrate, and contains always about 1 per cent of free nitric acid, which thus acts chemically upon the deposited silver (or acts to prevent its deposition to this extent, whichever way we wish to look at it).

(2) The weight dissolved, per 100 grams of anode corroded, is, assuming all the gold to appear in the slimes:

No. 1.

	Anode.	*Slimes.*	*Dissolved.*
Ag	98.69	0.03	98.66
Pb	1.09	....	1.09
Cu	0.12	....	0.12
Fe	0.09	....	0.09
Au	0.01	0.01	....

No. 2.

	Anode.	*Slimes.*	*Dissolved.*
Ag	74.08	0.14	77.94
Pb	3.71	0.01	3.70

	Anode.	*Slimes.*	*Dissolved.*
Cu	20.23	0.04	20.19
Fe	1.01	0.01	1.00
Au	0.05	0.05	....

The amount of current necessary to dissolve these weights will be the sum of the current which would be necessary to dissolve each constituent separately. These will be found in ampere-hours by dividing each by its electrochemical chemical equivalent $\times 3{,}600$.

No. 1.

		Ampere-Hours.
Ag	$98.66 \div 0.001118 \times 60 \times 60$	= 24.51
Pb	$1.09 \div 0.00107 \times 60 \times 60$	= 0.28
Cu	$0.12 \div 0.00033 \times 60 \times 60$	= 0.12
Fe	$0.09 \div 0.00029 \times 60 \times 60$	= 0.09
		25.00

No. 2.

Ag	$77.94 \div 4.025$	= 19.36
Pb	$3.70 \div 3.856$	= 0.96
Cu	$20.19 \div 1.185$	= 17.04
Fe	$1.00 \div 1.044$	= 0.96
		38.32

Since there is disposable $220 \times 24 = 5{,}280$ ampere-hours in a tank per day, there will be corroded the following weights of anodes per day in tanks containing Nos. 1 and 2, respectively;

No. 1..... $100 \times \frac{5{,}280}{25} =$ **21,120** Grams.

No. 2 $100 \times \frac{5{,}280}{38.32} =$ **13,779** "

(3) There are dissolved in a tank, per day, the following weights of silver:

No. 1 anodes: $21{,}120 \times 0.9866$	= 20,837	Grams
No. 2 anodes: $13{,}779 \times 0.7794$	= 10,739	"
Deposit in each tank	= 19,850	"
Surplus in No. 1 tank	= **987**	"
Deficit in No. 2 tank	= **9,111**	" (3)

(4) The heats of formation of the acid and salts concerned are:

(Ag, N, O^3, Ag)	= 23,000 cal.	=	213 cal. per gram Ag.	
(Pb, N^2, O^6, Ag)	= 98,200 "	=	474 " "	Pb.
(Cu, N^2, O^6, Ag)	= 81,300 "	=	1,278 " "	Cu.
(Fe, N^2, O^6, Ag)	= 43,900 "	=	784 " "	Fe.
(H, N, O^3, Ag)	= 48,800 "	=	48,800 " "	H

The heat balance per 100 grams of anodes No. 1 is:

Solution of Ag, 98.66 ×	213	= 21,015 cal.	
" Pb, 1.09 ×	474	= 517 "	
" Cu, 0.12 ×	1,278	= 153 "	
" Fe, 0.09 ×	784	= 71 "	
Heat evolved		=	**21,756** cal.
Deposition of Ag, 93.99 ×	213	= 20,020 "	
Liberation of H^2 0.06 ×	48,800	= 2,928 "	
Heat absorbed		=	**22,948** "
Heat deficit		=	**1,192** "

Since this is per 25 ampere-hours [see (2)] and 1 ampere hour at 1 volt = 860 calories, the voltage which this deficit of energy will absorb in the case of anodes No. 1 is:

$$1{,}192 \div 25 \div 860 = \mathbf{0.06} \text{ volt.} \qquad (4)$$

The similar calculation for anodes No. 2 gives per 100 grams corroded:

Solution of Ag, 77.94 ×	213	= 16,601 cal.	
" Pb, 3.70 ×	474	= 1,754 "	
" Cu, 20.19 ×	1,278	= 25,803 "	
" Fe, 1.00 ×	784	= 784 "	
Heat evolved		=	**44,942** cal.
Deposition of Ag, 98.11 ×	213	= 20,897 "	
Liberation of H^2 0.064 ×	8,800	= 2,928 "	
Heat absorbed			**23,825** "
Surplus heat		=	21,117 "
Voltage *generated*		=	**0.98** volt. (4)

(5) Resistance of each element of electrolyte of 1 square cm. area is $20 \times 4 = 80$ ohms. The current passing through this is $220 \div 10{,}000 = 0.022$ amperes. The drop of voltage, due to the resistance of the electrolyte, is, therefore,

$$0.022 \times 80 = 1.76 \text{ volts.}$$

Adding decomposition voltage we have

In case of No. 1 anodes, $1.76 + 0.06$	= 1.82 volts.	
Add for resistance of contacts	0.18 "	
Working voltage	2.00 "	(5)
In case of No. 2 anodes, $1.76 - 0.98$	= 0.78 "	
Add for resistance of contacts	0.18 "	
Working voltage	0.96 "	(5)

(6) Horsepower required per tank:

Anodes No. 1: $\frac{220 \times 2.00}{750}$ = 0.59 hp.

Anodes No. 2: $\frac{220 \times 0.96}{750}$ = 0.28 "

Power per kilogram of silver deposited:

Anodes No. 1, $0.59 \div 19.85$ = 0.020 hp-days
= **0.48** hp-hours. (6)

Anodes No. 2, $0.28 \div 19.85$ = 0.014 hp-days.
0.34 hp-hours. 6)

Problem 128.

The Wohlwill process for refining gold bullion operates with $AuCl^3$ solution, strongly acid with HCl. Design a plant for refining bullion having the analysis:

Au	60.3	Fe	2.2
Ag	7.0	Ni	2.0
Cu	6.5	Pb	7.0
Zn	15.0		

Assume the following data to start with:
Current density, 1,000 amperes per square meter.
Use ten tanks in series.
Tanks available, 500 mm. $\times$ 500 mm. $\times$ 300 mm. deep, inside.

Electrodes about 4 cm. apart.
Starting sheets 1 mm. thick.
Anodes 20 mm. thick.
Specific gravity of anodes 17.5.
Gold present in solution 50 grams per liter.
Specific resistance of electrolyte 5 ohms.
Specific gravity of the electrolyte 1.15.

Loss of electromotive force at contacts one-half the loss due to the resistance of the solution.

Anode products, $AuCl^3$, AgCl, CuCl, $ZnCl^2$, $FeCl^2$, $NiCl^2$, $PbCl^2$.

Required:

(1) The size and dimensions of electrodes and number in a tank.

(2) Current used and total voltage of the system.

(3) Gold deposited per day.

(4) Anodes corroded per day, assuming corrosion uniform.

(5) Deficit of gold in the tanks per day.

(6) If anodes are left in until 9/10 dissolved, how long will they last?

(7) If cathodes are removed every 24 hours, what is the average time of treatment?

(8) At 6 per cent per annum, what is the interest charge per kilogram of gold under treatment in the plant, gold being worth 72.9 cents per gram.

Solution:

(1) Allowing 1 cm. clearance at the sides, the plates must not be over 48 cm. in width across the tank. The electrolyte must not be nearer than 2 cm. to the top of the tank, and the plates ought to be 8 centimeters above the bottom, to allow space for slimes to accumulate. The immersed depth of plates is, therefore, 40 cm., and the superficial area 960 sq. cm. on a side.

With spaces 4 cm., anodes 2 cm. thick and cathodes 0.1 cm., using one more cathode than anode, we have the spaces equal in number to twice the anodes, and, therefore,

$(2 \times \text{anodes}) + (\text{anodes} + 1)\ 0.1 + (2\ \text{anodes} + 4) = 50$, whence the number of anodes figure out 4.9. (1)

Choosing the nearest whole number, 5, there will be 6 cathodes, and the working spaces will be 10, and their width

$$\frac{50 - 5(2) - 6(0.1)}{10} = \mathbf{3.94} \text{ cm.} \qquad (1)$$

(2) Ignoring the edges of the plates, the working surface per tank is $960 \times 2 \times 5 = 9{,}600$ sq. cm., and the current $9{,}600 \div 10{,}000 \times 1{,}000 = \mathbf{960}$ amperes. (2)

The voltage to overcome ohmic resistance is

$$5 \times 3.94 \times \frac{1{,}000}{10{,}000} = 1.97 \text{ volts.}$$

Add 50 per cent loss at contacts = 0.98 "

Sum = 2.95 "

The voltage corresponding to the chemical action occurring can be calculated from the energy of formation of the $AuCl^3$ decomposed minus the energy of formation of the salts formed. More simply, although not so logically, it may be derived from the voltages of decomposition of these compounds, allowing for the proportions of each formed and decomposed. These are:

(Au, Cl^3)	=	$27{,}200 \div 3 \div 23{,}040$	= 0.393 volt.
(Ag, Cl)	=	$29{,}000 \div 1 \div 23{,}040$	= 1.257 "
(Cu, Cl)	=	$35{,}400 \div 1 \div 23{,}040$	= 1.536 "
(Zn, Cl^2)	=	$113{,}000 \div 2 \div 23{,}040$	= 2.448 "
(Fe, Cl^2)	=	$100{,}100 \div 2 \div 23{,}040$	= 2.170 "
(Ni, Cl^2)	=	$93{,}900 \div 2 \div 23{,}040$	= 2.037 "
(Pb, Cl^2)	=	$77{,}900 \div 2 \div 23{,}040$	= 1.690 "

These are the voltages which would be generated at the anode in case each one of these salts was the only salt being formed. But, since we know the exact composition of our anode dissolved, we can calculate the corresponding voltage generated at the anode:

Au,	0.603×0.393	= 0.237 volt.
Ag,	0.070×1.257	= 0.088 "
Cu,	0.065×1.536	= 0.101 "
Zn,	0.150×2.448	= 0.367 "
Fe,	0.022×2.170	= 0.048 "

Ni, 0.020×2.037	= 0.041	volt.
Pb, 0.070×1.690	= 0.118	"
Sum	1.000	"
Absorbed at the cathode	0.393	"
Total voltage generated	0.607	"
Absorbed in electrolyte and connections	2.95	"
Working voltage per tank	2.34	"
Total for the system	**23.4**	" (2)

(3) Au deposited by 960 amperes in ten tanks per day:

$$0.00001035 \times \frac{197}{3} \times 60 \times 60 \times 24 \times 960 \times 10 = 563{,}729 \text{ gr.}$$
$$= 563.729 \text{ kg.}$$

(4) One gram of anode requires for its corrosion:

Au,	$0.603 \div 197$	$\div 3 \div 0.00001035$	
Ag,	$0.603 \div 108$	$\div 0.00001035$	
Cu,	$0.065 \div 63.6$	$\div 0.00001035$	
Zn,	$0.150 \div 65$	$\div 2 \div 0.00001035$	
Fe,	$0.022 \div 56$	$\div 2 \div 0.00001035$	
Ni,	$0.020 \div 59$	$\div 2 \div 0.00001035$	
Pb,	$0.070 \div 207$	$\div 2 \div 0.00001035$	
	$= 0.01703$	$\div 0.00001035$	$= 1{,}645$ amp. seconds.

Current available per day:

$960 \times 60 \times 60 \times 24 \times 10 = 829{,}440{,}000$ amp. seconds.

Anodes corroded per day:

$829{,}440{,}000 \div 1{,}645 = 504{,}220$ grams.

	=	**504.220**	kilograms (4)
(5) Gold deposited	=	563.729	"
Gold dissolved = 504.220×0.603	=	304.045	"
Deficit of gold in the plant per day	=	**259.684**	" (5)

(6) Weight of anodes:

$960 \times 4 \times 17.5 \times 5 \times 10$	=	3,360,000	grams.
	=	3,360	kilograms.
One-tenth scrap	=	336	"
Weight corroded	=	3,024	"

Days to corrode them:

$$\frac{3,024}{504.22} = \mathbf{5.93} = \text{practically } \mathbf{6} \text{ days.} \qquad (6)$$

(7) Average time of treatment, removing one-sixth each day:

$$(1+2+3+4+5+6) \div 6 = \mathbf{3.5} \text{ days.} \qquad (7)$$

(8) Value of gold in plant is, in regular running, value of cathodes for all the time plus value of anodes for $3.5 \div 6 = 58$ per cent of the time.

Value of cathodes:

$960 \times 0.1 \times 19.2$ (sp. gr. gold) $\times 6 \times 10 \times 0.729 = \$80,578$

Value of gold in anodes:

$3,360,000 \times 0.603 \times 0.729 = 1,477,012$

Average value of anode gold under treatment:

$1,477,012 \times (3.5 \div 6) = 861,590$

Sum of cathode gold continually in stock and average value of anode gold under treatment:

$80,578 + $861,590 =	$942,168
Interest per annum at 6 per cent =	56,530
Interest charge per day =	155

Interest charge per kg. of anode refined:

$\$155 \div 504.22 =$ $0.31 per kg.

Interest charge per kg. of gold under treatment:

$\$155 \div 304.045 =$ **$0.51** per kg. (8)

The Volatilization of Silver and Gold.

It is known that both of these metals can be vaporized; it can easily be done in the electric arc. If they are placed in a vacuum, in quartz vessels, they show signs of metal vaporizing at 680° and 1,070°, respectively, although what vapor tension this corresponds to we do not exactly know, but we can surmise it to be a small fraction of a millimeter. If heated still higher in a vacuum, they show the phenomenon of ebullition, or boil, at 1,360° and 1,800°, respectively, although here again we do not know what pressure this corresponds to,

except it is the pressure of the melted metals above the spot where the vapor commences to form beneath the surface, which might be 5 to 10 millimeters of melted metal, say 10 millimeters of mercury, if the bath of metal were shallow.

From these data, obtained by Schuller, Krafft and Bergfeld, it is estimated that the boiling points of the two metals under atmospheric pressure are 2,040° and 2,530°, respectively, on the assumption that the temperature interval between first signs of vaporization in a vacuum and boiling in a vacuum is equal to the interval between the latter temperature and the ordinary boiling point. (This is said to be true of mercury.)

O. P. Watts has estimated the boiling point of silver and gold as 1,850° and 2,800°, respectively, meaning probably at atmospheric pressure; but his estimate is based on such assumptions that they cannot lay claim to as much accuracy as the data and estimates above cited.

If we go back to the very probable rule, that at equal fractions of the normal boiling points, expressed in absolute temperatures, metals have the same vapor tensions, we can compare silver and gold with mercury, whose vapor tension is known through a wide range, and get quite probable values for the vapor tensions of these metals through a large range of temperature. The following table is from nearly zero tension to about the temperature at which ebullition is noticeable in a vacuum:

Tension of Vapor. mm. of Hg.	*Mercury. C°*	*Lead. C°*	*Silver. C°*	*Gold. C°*
0.0002	0	625	729	942
0.0005	10	658	766	987
0.0013	20	691	802	1,031
0.0029	30	724	839	1,075
0.0063	40	757	876	1,120
0.013	50	790	913	1,165
0.026	60	822	949	1,209
0.050	70	855	986	1,254
0.093	80	888	1,023	1,298
0.165	90	921	1,059	1,343
0.285	100	954	1,096	1,387

Tension of Vapor. mm. of Hg.	*Mercury. C°*	*Lead C°*	*Silver. C°*	*Gold. C°*
0.478	110	987	1,133	1,432
0.779	120	1,020	1,169	1,476
1.24	130	1,053	1,206	1,520
1.93	140	1,086	1,243	1,565
2.93	150	1,119	1,280	1,611
4.38	160	1,151	1,316	1,654
6.41	170	1,184	1,353	1,699
9.23	180	1,217	1,390	1,743

Inspecting the above table, we see that apparently about 0.0002 mm. of mercury tension is sufficient to make a metal show signs of vaporization. The corresponding temperatures at which silver and gold show 0.0002 mm. tension are, from the above table, 729° and 942°, respectively, whereas it is said to have been observed for these metals at 680° and 1,070°. The divergence is not wide, considering the lack of exact data involved.

Mercury is said to show ebullition in a vacuum at 180°, lead at 1,250°, silver at 1,360° and gold at 1,800°. From the above table we see these metals having the same vapor tension at 180°, 1,217°, 1,390°, and 1,743°, respectively. The agreement is encouraging.

The table in continuation is for temperatures from those causing ebullition in a vacuum to those required to boil the metals at atmospheric pressure:

Tension of Vapor. mm. of Hg.	*Mercury. C°*	*Lead. C°*	*Silver. C°*	*Gold. C°*
9.23	180	1,217	1,390	1,743
14.84	190	1,250	1,427	1,788
19.90	200	1,283	1,463	1,832
26.35	210	1,316	1,500	1,877
34.70	220	1,349	1,537	1,921
45.35	230	1,382	1,574	1,965
58.82	240	1,415	1,610	2,010
75.75	250	1,448	1,647	2,055
96.73	260	1,480	1,684	2,099

Tension of Vapor. mm. of Hg.	*Mercury.* C°	*Lead.* C°	*Silver.* C°	*Gold.* C°
123.	270	1,513	1,720	2,144
155.	280	1,546	1,757	2,188
195.	290	1,579	1,794	2,233
242.	300	1,612	1,830	2,277
300.	310	1,645	1,867	2,322
369.	320	1,678	1,904	2,366
451.	330	1,711	1,941	2,410
548.	340	1,744	1,977	2,455
663.	350	1,777	2,014	2,500
760.	**357**	**1,800**	**2,040**	**2,530**

For tensions of metallic vapors over 1 atmosphere, such as may easily occur in high temperature work, particularly in electric furnaces, the following data may be useful:

Tension of Vapor. Atmospheres.	*Mercury.* C°	*Lead.* C°	*Silver.* C°	*Gold.* C°
1.0	357	1,800	2,040	2,530
2.1	400	1,951	2,197	2,722
4.25	450	2,116	2,380	2,945
8.	500	2,280	2,564	3,167
13.8	550	2,445	2,747	3,390
22.3	600	2,609	2,931	3,612
34.0	650	2,774	3,114	3,835
50.	700	2,938	3,298	4,057
72.	750	3,103	3,481	4,280
102.	800	3,267	3,665	4,502
137.5	850	3,436	3,848	4,725
162.	880	3,525	3,958	4,858

The last table may not be of much immediate practical value, but it is interesting scientific information. The preceding tables are, however, technically and commercially important. They point particularly to the wastefulness of melting silver or gold in open furnaces where furnace gases pass over the metal. Such gases, at temperatures above 700° for silver and 950° for gold, *i.e.*, even passing over *unmelted* metal, can cause volatilization and loss of weight, because they

evaporate the metal on exactly the same principle that a current of dry air evaporates ice or water. They also explain why silver volatilizes with lead in the cupellation operation. At 1,000° C. lead has a vapor tension of about 0.62 mm. of mercury, and silver about 0.07 mm., and therefore, a considerable loss of silver is sure to occur with the lead vapors passing off. Gold at the same temperature has only 0.0007 mm. tension, and, therefore, proportionately less of it is lost, say only one-fiftieth as much as the silver loss, reckoning from the proportionate tensions and the relative densities of the two vapors.

In calculating such metallic vapor losses it is important to remember that the metals are monatomic when in the state of vapor, and that the molecular weights of their vapors are simply their atomic weights. The hypothetical weight of a cubic meter of such metallic vapor at standard conditions, 0° C. and 760 mm. pressure, is therefore,

$$0.09 \text{ kg.} \times \frac{\text{atomic weight}}{2},$$

and from this theoretical datum the weight of *any* volume at *any* temperature and *any* tension can be calculated.

Illustration: Calculate the weight of silver vapor contained in 1 cubic meter of furnace gases, if saturated with silver vapor and at 1,100° C.

Solution: Since the tension of silver at this temperature is 0.28 mm., the question resolves itself into this: What is the weight of 1 cubic meter of silver vapor at 1,100° and 0.28 mm. pressure. One cubic meter at standard conditions would be $0.09 \times (108 \div 2) = 4.86$ kilograms; therefore, at these given conditions, it contains:

$$4.86 \times \frac{273}{1{,}100+273} \times \frac{0.28}{760} = \mathbf{0.0035} \text{ kg.}$$

$$= 3.5 \text{ grams.}$$

It is true that the silver vapor, being heavy, mixes slowly with the furnace gases, but, nevertheless, the gases rushing over and coming in contact with the silver may become nearly saturated with this vapor, and carry considerable away. In

the Bessemerizing of copper matte to blister copper, by blowing air directly through it, as much as 30 per cent of all the silver present may be thus vaporized from the bath as soon as the silver has taken the metallic form.

Every smelter and refiner of the precious metals should be familiar with these facts, and draw conclusions from them useful to the conduct of his business.

The specific heat of these metallic vapors is 0.225 per cubic meter (calculated to standard conditions), and the latent heat of vaporization is approximately twenty-three times the normal boiling point expressed in absolute temperature for one atomic weight of the metal—as explained in Part I of these calculations.

For silver and gold we would have the latent heats:

Ag, 23 (2,040+273)	= 53,200	Cal. per	108 kg.
	= **493**	"	1 kg.
Au, 23 (2,530+273)	= 64,470	"	197 kg.
	= **327**	"	1 kg.

The above latent heats of vaporization are for boiling at normal atmospheric pressure; for vaporization at other pressures and corresponding temperatures, correction must be made for the difference in specific heats of the metallic vapor and liquid metal.

CHAPTER IV.

THE METALLURGY OF ZINC.

(Including Cadmium and Mercury.)

At the present time, the metallurgy of zinc is briefly comprehended in the following statements: The chief ore is zinc sulphide, ZnS, infusible at ordinary furnace heats, non-volatile, easily roasted to ZnO; the roasting is done principally in mechanically stirred furnaces, the ore being in small pieces, because it is non-porous, compact, and roasts slowly; the roasted ore, principally ZnO, is mixed with an excess of carbon as a reducing agent, and heated in closed fire-clay retorts having condensers attached; zinc vapors begin to come off at 1033° C., and come off rapidly at the working temperature of the charge, say 1200° to 1300°; the zinc vapor and carbon monoxide pass into the condensers, and as they cool deposit the zinc, some in the form of fine dust (like hoar frost), most of it as liquid drops; the cadmium in the ore and some lead, if present, distil over with the zinc, constituting its chief impurities. Arsenic is sometimes present in the condensed product. Iron does not distil over, but some is absorbed from ladles and moulds in which the liquid zinc may be handled and cast.

The chief operations with which calculations may be concerned are the roasting, reduction by carbon, condensation of the vapors, possibility of blast-furnace extraction, of electric furnace reduction, electrolytic extraction, electrolytic refining.

Roasting of Sphalerite.

Before roasting, the crude ore is crushed and concentrated. Pure ZnS contains 67 per cent zinc and 33 per cent sulphur; its specific gravity is 3.9 and it has fine cleavage, so that it crushes easily, producing much fines or slimes. In the Joplin district, in Missouri, the largest zinc field in America, the ore as mined averages some 4.3 per cent of zinc, equal to 6.4 per cent of pure blende, ZnS, and is concentrated by jigging to

heads carrying about 60 per cent of zinc (90 per cent of ZnS), containing some 70 per cent of the zinc in the ore, and tails carrying about 1.35 per cent of zinc (2 per cent of ZnS), representing 30 per cent of the zinc in the ore. The concentrates average 5 per cent of the weight of the ore; concentration ratio 20 to 1. Cost of such crushing and concentration 20 to 40 cents per ton of ore milled. (Ingalls.) The average composition of these concentrates is:

Zinc.....	60 per cent	=	90 per cent ZnS.
Iron.....	2 "	=	3 per cent FeS.
Silica.....	7 "		
Sulphur.....	31 "		
	100		

Zinc sulphide begins to be oxidized by air at a dull red heat, say, 600° C., and if the supply of air is kept up the oxidation is rapid, generating a large amount of heat and consequent high temperature.

$$2ZnS + 3O^2 = 2ZnO + 2SO^2$$

The question as to how high a temperature would theoretically result if sphalerite were thus burned is an interesting one. Ingalls quotes Hollaway as giving 1992° C. We will investigate this point as being of interest and value in connection with practical roasting.

Problem 129.

Pure ZnS is oxidized by air. The heats of formation concerned are:

$$(Zn, S) = 43{,}000$$
$$(Zn, O) = 84{,}000$$
$$(S, O^2) = 69{,}260$$

The specific heats of the materials concerned are:

	Sm to O°
Zn S	= 0.120 +0.00003t
Zn O	= 0.1212+0.0000315t
$S O^2$ (1 m^3)	= 0.36 +0.0003t
O^2 or N^2 (")	= 0.303 +0.000027t

Assuming that the blende is first heated to 600°, to start the roasting, and then the air supply put on, the exposed roasting

surface being sufficient for rapid oxidation, and the temperature too high to form SO^3:

Required:

(1) The theoretical temperature at the roasting surface at starting, if all the oxygen passing is utilized.

(2) The same, when the operation has continued to its maximum temperature.

(3) The same, if three-fourths the oxygen passing is utilized.

(4) The same, if half the oxygen passing is utilized.

(5) The same, if the resulting gases contain only 5 per cent of SO^2 gas.

Solution:

(1) The reaction gives, thermally:

Decomposition of ZnS	—43,000 Cal.
Formation of ZnO	+84,800 "
" " SO^2	+69,260 "
Net heat evolution	111,060 Cal.

This would be concerned in the oxidation of 97 kg. of ZnS to 81 kg. of ZnO and 64 kg. of SO^2 (= 22.22 m^3), and requiring $3 \times 16 = 48$ kg. of $O^2 = 208$ kg. of air (containing 160 kg. = 127 cubic meters of N^2).

Heat in 97 kg. of ZnS at 600°	= 8,032 Cal.
Total heat in the products	= 119,092 "

Mean heat capacity of the products per 1°, from 0° to t°:

81 kg. ZnO	= 9.8172 + 0.002552t
22.22 m^3 SO^2	= 8.0000 + 0.006667t
127 m^3 N^2	= 38.4810 + 0.003429t.
Sum	= 56.2982 + 0.012648t

Therefore, theoretical surface temperature, at starting,

$$t = \frac{119{,}092}{56.2982 + 0.012648t} = \mathbf{1565}^\circ \text{ C.} \qquad (1)$$

(2) When the surface of the oxidizing material has attained its maximum temperature, it is practically at t°, and the products of combustion will contain 111,060 Calories plus the heat in 97 kg. of ZnS at t°. We then have

$$t = \frac{111{,}060 + 11.24t + 0.00291t^2}{56.2982 + 0.012648t} = \mathbf{1780°}. \qquad (2)$$

It must be emphasized that this is the theoretical maximum under the most favorable conditions as to oxidation and exact air supply, conditions never realized in practice.

(3) The excess of oxygen would be $48 \times \frac{1}{3} = 16$ kg. $= 11.11$ m³. This would be the most favorable possible proportion for making sulphuric acid from the gases, since it would just serve to oxidize the SO^2 to SO^3 in the acid chambers, the complete reactions being:

Roasting $- ZnS + 2O^2 = ZnO + SO^2 + O$
Acid chambers $- SO^2 + O = SO^3$.

The 11.11 m³ of oxygen corresponds to 53.4 m³ of excess air, whose mean heat capacity is $16.1903 + 0.001443t$. Adding this to the mean heat capacity of the products we have:

$$t = \frac{111{,}060 + 11.24t + 0.00291t^2}{72.4885 + 0.014091t} = \mathbf{1437°} \qquad (3)$$

(4) This is more nearly the practical conditions, and applying the principles above explained, we have:

$$t = \frac{111{,}060 + 11.24t + 0.00291t^2}{104.8691 + 0.016977t} = \mathbf{1027°} \qquad (4)$$

(5) If the gases contain 5 per cent of SO^2 gas, their total volume per formula weight of SO^2 produced, in kilograms, is:

$$22.22 \div 0.05 = 444.4 \text{ m}^3$$

and the volume of excess air they contain is:

$$444.4 - 22.2 - 127 = 295.2 \text{ m}^3$$

the heat capacity of this excess air, per average 1° is:

$$89.4456 + 0.007970t$$

and

$$t = \frac{111{,}060 + 11.24t + 0.00291t^2}{145.7438 + 0.024947t} = \mathbf{731°} \qquad (5)$$

It follows from this analysis and these results, that effective auto-roasting of zinc sulphide is practicable provided that the ore is finely divided, so as to expose large surface, oxidize quickly, and utilize the oxygen of the air efficiently. Without these conditions, auto-roasting is impracticable.

It ought to roast satisfactorily by pot roasting, if the proper conditions as to size of ore, speed of blast, thickness of pot walls, etc., can be found.

Problem 130.

Average blende concentrates, containing 90 per cent ZnS, 3 per cent FeS, 7 per cent SiO^2, are roasted by the use of 30 per cent of coal, in a furnace with a hearth 135 feet effective length, the unroasted sphalerite remaining being 2.6 per cent of the roasted material. The iron is roasted to Fe^2O^3. The coal carries 75 per cent of carbon, 5 per cent of hydrogen, 8 per cent of oxygen, 1 per cent of sulphur and 11 per cent of ash. The chimney gases average 2 per cent of SO^2 and escape from the furnace at 300° C. Charge is drawn from the furnace at 1000° C. Furnace roasts 40,000 pounds per day. Width of furnace, 12 feet; height, 8 feet.

Required:

(1) The composition of the roasted ore.

(2) The heat generated by the roasting of 2,000 pounds of the ore.

(3) The heat generated by the combustion of the fuel.

(4) The heat in the hot charge as drawn.

(5) The heat in the chimney gases.

(6) The heat lost by radiation and conduction.

(7) The heat loss calculated to pound-calories per square foot of outer surface per minute.

Solution:

(1) The 2.6 per cent of ZnS in the roasted ore is per cent of it, and not of the raw ore. The simplest method of getting the composition of the roasted ore is to represent by x the quantity of ZnS remain unoxidized per 100 of raw ore. We then have:

Weight of ZnS oxidized, per 100 raw ore $= 90 - x$

" " ZnO formed $= (90 - x) \times \frac{81}{97} = 75.2 - 0.835\,x$

" " Fe^2O^3 " $= 3 \times \frac{160}{176} = 2.7$

Weight of SiO^2 remaining = 7.0
" " roasted ore = $84.9 - 0.835\,x$
" " " " also = $x \div 0.026$

Therefore

$$84.9 - 0.835\,x = x \div 0.026$$

Whence

$$x = 2.2$$

Percentage of the ZnS oxidized

$$\frac{90 - 2.2}{90} = 0.976 = 97.6 \text{ per cent.}$$

Composition and weight of the roasted ore:

ZnS	= 2.2 =	2.6 per cent.
ZnO	= 73.4 =	86.1 "
Fe^2O^3	= 2.7 =	3.1 "
SiO^2	= 7.0 =	8.2 "
Weight	**85.3**	

Zinc contents = 60.0 = **70.3** per cent. (1)

(2) Zinc sulphide oxidized to ZnO

$2000 \times (0.90 - 0.022)$ = 1,756 lbs.

Heat of oxidation of 97 lbs. of ZnS to ZnO and SO^2 (from Prob. 129) = 111,060 lb.-Cal.
Heat of oxidation of 1 lb. = 1,145 " "
" " " " 1,756 lbs. = 2,010,620 " " (2)

(3) Heat of combustion of 1 lb. of fuel to CO^2 and H^2O vapor:

C to CO^2 0.75×8100 = 6075 lb.-Cal.
Available Hydrogen
$0.05 - 0.01 = 0.04$
H to H^2O condensed
$0.04 \times 34{,}500$ = 1380 " "
Calorific power to H^2O condensed = 7455 " "
Water formed
$0.05 \times 9 = 0.45$
Latent heat of condensation
0.45×606.5 = 273 " "
Calorific power to H^2O vapor = 7182 " "

Coal used per 2000 lbs. of ore = 600 lbs.
Calorific power = 600×7182 = 4,309,200 lb.-cal.

(3)

Total heat generated in the furnace
$2{,}010{,}620 + 4{,}309{,}200$ = 6,319,820 " "

Proportion of total generated by the roasting
$2{,}010{,}620 \div 6{,}319{,}820 = 0.325 = 32.5$ per cent.

(4) Charge, as drawn, per 2000 lbs. of raw ore:

ZnS	44 lb.
ZnO	1468 "
Fe^2O^3	54 "
SiO^2	140 "
	1706 "

Heat in this, at 1,000° C.

ZnS	44×0.150	= 6.6
ZnO	1468×0.153	= 224.6
Fe^2O^3	54×0.344	= 18.0
SiO^2	140×0.260	= 36.4

285.6×1000 = 285,600 lb.-Cal.

(4)

(5) Sulphur going into the gases:

S from ZnS	$1756 \times 32/97$	=	579.4 lb.
S " FeS	$60 \times 32/88$	=	21.8 "
S " coal	600×0.01	=	6.0 "
Weight of S		=	607.2 "
" " O for SO^2		=	607.2 "
" " SO^2			1214.4 "

Volume of SO^2—
$(1214.4 \times 16) \div 2.88$ = 6,747 cubic feet.

Volume of chimney gas—
$6{,}747 \div 0.02$ = 337,350 " "

Volume of CO^2 in it—
$(600 \times 0.75 \times 16) \div 1.98$ = 3,636 " "

Volume of H^2O in it—
$(600 \times 0.45 \times 16) \div 0.81$ = 5,333 " "

Volume of N^2 and excess air = 321,634 " "

Heat in these gases at 300° C.

CO^2	$3,636 \times 0.436$	=	1,585	oz.-cal.	per	1°
H^2O	$5,333 \times 0.385$	=	2,057	"	"	"
SO^2	$6,747 \times 0.450$	=	3,036	"	"	"
N^2 and O^2	$321,634 \times 0.311$	=	100,028	"	"	"
			106,706	"	"	"
		=	6,669 lb.-Cal.		"	
		=	2,000,700	"	"	300° (5)

(6) Summary of heat distribution:

Heat available, per 2,000 lb. ore = 6,319,820 lb.-Cal.

Heat in hot ore drawn,	235,600	"	"
" " chimney gases,	2,000,700	"	"
Loss by radiation and conduction,	4,083,620	"	"
	6,319,820	"	" (6)

(7) Approximate periphery of furnace:

$$12+12+8+8 = 40 \text{ feet.}$$

Approximate outer surface, including base:

$$40 \times 135 = 5,400 \text{ sq. feet.}$$

Ore roasted per hour:

$$40,000 \div 24 = 1,667 \text{ lb.}$$

Heat radiated and conducted away per hour:

$$\frac{4,083,520}{2,000} \times 1,667 = 3,360,000 \text{ lb.-Cal.}$$

Per square foot outside area, per hour:

$$3,360,000 \div 5,400 = 622 \text{ lb.-Cal.}$$

per minute = **10.5** " " (7)

Reduction of Zinc Oxide.

Since metallic zinc boils under atmospheric pressure at 930° C., and carbon does not begin to reduce zinc oxide until 1033° is reached, the zinc reduced is necessarily obtained in the state of vapor. To make the reaction proceed fast, a temperature of the charge inside the retorts of 1100° to 1300° C. at the end

is necessary. A large amount of heat is absorbed in the reaction, which must be supplied as a current or flow of heat through the walls of the retort in order to keep the reaction and reduction going. Since the walls of the retort are fire-clay, averaging 4 centimeters (1.6 inch) thick, there must be a considerable difference of temperature (temperature head) between the inside and outside of the retort in order to keep up the flow of heat inward.

Thermochemical Considerations.

The heat of formation of zinc oxide, at ordinary temperatures, is 84,800 Calories for a molecular weight, 81 kilos, of oxide, as determined by thermochemical experiment. This means that cold zinc uniting with cold oxygen, and the hot product cooled down to the same starting temperature, results in the evolution of heat stated. Cold carbon uniting with cold oxygen to cold carbonous oxide, CO, gives similarly 29,160 Calories per molecular weight, 28 kilograms, of gas formed. These facts are expressed thermochemically as

$$(Zn, O) = 84,800$$
$$(C, O) = 29,160$$

The equation of reduction becomes

$$ZnO + C = Zn + CO$$
$$-84,800 \qquad +29,160 = -55,640$$

This means that if we start with cold zinc oxide and cold carbon, the heat absorbed is 55,640 Calories ending up with cold products, zinc and CO at ordinary temperatures.

What is actually done in practice, however, is to first heat the ZnO and C to a high temperature, at least to 1033°, and then to supply the heat of the reaction at that temperature, producing zinc vapor and CO gas, both at 1033°. The process of reduction, therefore, resolves itself plainly into two steps: (1) heating the charge up to the reacting temperature, (2) supplying the latent heat of the chemical change at that temperature.

Heating up the Charge.

The charge usually contains more carbon than is theoretically necessary for reduction of the zinc oxide, because some is consumed by air in the retort, some in reducing iron oxides and

some is left behind unused; it is cheaper to lose carbon than unreduced zinc oxide. However, making the calculation on the theoretical amount of carbon only (anyone can modify it for any excess of carbon used in any specific case) we need to know the heat necessary to raise these reacting substances to the temperature of reaction.

The heat in 1 kilogram of zinc oxide at various temperatures was determined in the writer's laboratory as $0.1212t + 0.0000315t^2$. The heat in 1 kilogram of carbon at temperatures above 1000° is represented by $0.5t - 120$. We have the heat necessary to raise our 81 kilograms of ZnO and 12 kilograms of carbon to 1033° as

$$\begin{aligned} \text{ZnO} : 0.1212\ (1033) + 0.0000315\ (1033)^2 \times 81 & \\ = 159 \times 81 = 12{,}879 \text{ Cal.} & \\ \text{C} : [0.5\ (1033) - 120] \times 12 = 396 \times 12 = 4{,}752 \text{ "} & \\ \text{Sum} = 17{,}631 \text{ "} & \end{aligned}$$

This quantity represents the heat per 81 of oxide and 12 of carbon, or 93 of charge containing 65 of zinc. Per 1000 kilograms of oxide, containing 800 kilos of zinc, it would be

$$17{,}631 \times \frac{1000}{81} = 217{,}670 \text{ Calories.}$$

It should be noted that this quantity is actually proportional to the weight of the charge, ore plus reducing agent, and independent of the amount of zinc in it. A ton of poor ore will practically require as much heat to bring it up to the reaction temperature as a ton of rich ore, so that these costs are proportional to the weight of charge treated and not to the weight of zinc it contains.

If the charge is heated electrically, the amount of electric power needed for heating up can be calculated, assuming an average loss of 10 to 30 per cent of the total heat by radiation and conduction from the furnace.

Illustration:

A retort contains 300 kilograms of charge mixture and is heated electrically to 1033°, the reaction temperature at an efficiency of 75 per cent, by an electric current of 250 horse-power. How long will the heating-up period last.

Solution:

Heat needed in the charge, $217,670 \times 0.3 = 65,300$ Calories. Heat to be supplied $= 65,300 \div 0.75 = 87,070$ Calories. Power applied supplies $635 \times 250 = 158,750$ Calories per hour. Time required $87,070 \div 158,750 = 0.55$ hour $= 33$ minutes.

If the charge is heated by furnace gases outside the retort we must take into consideration that the fire-clay is a poor conductor, that the rate of transmission of heat through the walls falls off as the charge becomes hot, and that the outside surface of the retort must be kept well above 1033° in order to get the charge to that temperature in a reasonable time. The conductance of fire-clay for high temperature is 0.0031; that is, 0.0031 gram-calories pass through each square centimeter per second, if one centimeter thick, per 1° C. difference of temperature. When the charge is cold, the inner surface of the retort may be reduced in temperature to a low red heat, say, 500°, and towards the end of the heating-up period its temperature becomes at least 1033°, while the outer surface is kept continually at 1200°, let us say, by the furnace gases. During the heating-up period there is a difference of temperature producing heat flow of 700°, for a short time, down to, say, 200°, which we may average up as 300° heat difference. The heat conductivity of the material of the retort and the thickness of its walls have everything to do with the rate at which the heat can get through and the charge be heated up to the reaction temperature.

Problem 131.

An oval zinc retort is 130 centimeters long, 30 centimeters diameter outside, one way, and 15 centimeters the other, and its walls are 3 centimeters thick. It is charged with 30 kilograms of ore and 12 kilograms of reduction material. The temperatures of the charge in the retort and of the gases outside the retort were as follows:

	In Retort	Outside	Difference
At starting.	0°C.	1067°C.	1067°C.
In 0.5 hour	350	1067	717
" 1.0 "	600	1067	467
" 1.5 hours	781	1067	286
" 2.0 "	814	1100	286

	In Retort	Outside	Difference
" 2.5 "	869	1100	231
" 3.0 "	924	1110	187
" 3.5 "	957	1155	198
" 4.0 "	935	1166	231
" 4.5 "	935	1138	203
" 5.0 "	946	1144	198
" 5.5 "	946	1155	209
" 6.0 "	979	1166	187
" 6.5 "	1001	1177	176
" 7.0 "	1034	1177	143
			Average, 319

Take 159 Calories per kg. as the heat required to bring the ore to 1034° and 396 for the reduction material.

Required:

The average heat conductivity in C. G. S. units of the material of the retorts, in the range given, assuming the inner surface of the retort to be at the same temperature as the charge.

Solution:

Heat passing through the retort walls in 7 hours:

$$159 \times 30 = 4770 \text{ Calories}$$
$$396 \times 12 = 4752 \text{ "}$$
$$9522 \text{ "}$$
$$\text{Per second} = 0.378 \text{ "}$$
$$= 378 \text{ gram-cal.}$$

Surface of retort:

$$\text{Periphery} \quad \sqrt{30 \times 15} \times 3.14 = 66 \text{ cm.}$$
$$\text{Area of sides,} \quad 66 \times 130 = 8580 \text{ sq. cm.}$$

Heat passing through each square cm. per second

$$378 \div 8580 = 0.044 \text{ cal.}$$

Heat passing per 1° difference

$$0.044 \div 319 = 0.00014 \text{ cal.}$$

Since thickness is actually 3 centimeters, conductance in C. G. S. units is:

$$0.00014 \times 3 = 0.00042.$$

Correction:

This coefficient of conductance is far too low. The reason is that the inner temperature, the temperature of the charge, is always lower than the temperature of the inside surface of the retort, and the difference of temperature between the outer and inner walls of the retort must have been far less than the average, 319°. If we take the coefficient of conductance as determined by experiment for firebrick, viz., 0.0031, then the average difference of temperature between the inner and the outer walls of the retort would be:

$$319 \times \frac{0.00042}{0.0030} = 45° \text{ C.}$$

This is more likely, than that the conductance of the retort material should be so extraordinarily low. In fact, we are led to the conclusion that the poor heat conductivity of the charge itself is the chief obstacle to its rapid heating, and that preheating of the charge would be very advisable if it could be done by some of the waste heat of the gases leaving the furnace.

Distillation of the Charge.

The driving off of the zinc is altogether a different operation from the heating up of the charge to the stated reduction temperature. It is an endothermic chemical operation, comparable to the boiling of water at a constant temperature, the latent heat of the chemical reaction is exactly comparable to the latent heat of vaporization. The temperature must be kept up to the temperature of reduction in order for the reaction to take place at all, and then heat-calories must be supplied at that temperature to keep the reaction going, and the reduction proceeds *pari passu* with the *quantity* of heat supplied at that constant temperature. The question now is: what is the latent heat of this reaction at the reaction temperature.

We must for this purpose know the heat of formation of the substances involved, ZnO and CO, at 1033°. The method of calculating these is too long to insert here, but may be learned from the writer's book on Metallurgical Calculations, Part I, p. 51. We have the heats of formation from the elements as they exist at 1033°:

$$(Zn, O)^{1033} = 112,580$$
$$(C, O)^{1033} = 30,091$$

and the reaction at 1033°

$$ZnO + C = CO + Zn$$
$$-112,580 + 30,091 = -82,489$$

This is seen to be nearly 50 per cent greater than the heat of the reaction calculated to ordinary temperatures, from the ordinary heats of formation as taken from thermochemical tables. The metallurgist should understand this difference, for it is one of the utmost importance in thermochemical calculations, if we want our calculations to represent actual conditions and to check up with practice.

This amount of heat is proportional to the zinc oxide reduced or to the zinc distilled from the charge, but not to the weight of ore charge itself. This requirement will, therefore, be greater, per retort full of material, the richer the charge is in zinc. It is a constant requirement for a given output of zinc, and not per given weight of ore treated.

The heat required for the reduction, therefore, as distinguished from the heating-up period, is

$$\frac{82,489}{81} = 1,018 \text{ Calories per kg. of ZnO reduced}$$

$$\frac{82,489}{65} = 1,269 \text{ " " " " " Zn distilled off}$$

$$= 1,269,000 \text{ " " ton " " " "}$$

Furnishing this reduction heat, at the high temperature required, is the larger part of the heat needed in the whole process. We see that it is some 4.7 times the amount of heat needed to raise the materials to the reduction temperature.

Problem 132.

The retort charge of Problem 131 was kept at the reduction temperature for 14 hours, the temperature outside the retort being gradually raised to 1300° and the average difference in temperature between the gases and the charge being 147°, and there being distilled from the charge in that time 18 kilograms of zinc.

Required:

The average heat conductance in C. G. S. units of the material of the retort from the above data and assumptions.

Solution:

The heat furnished in the 14 hours was as follows:

$$1{,}269 \times 18 = 22{,}842 \text{ Calories.}$$

Heat furnished per hour:

$$22{,}842 \div 14 = 1{,}632 \quad "$$

Heat furnished per second:

$$= 0.453 \quad "$$
$$= 453 \text{ calories}$$

Heat passing each sq. cm. of retort surface per second:

$$453 \div 8{,}580 = 0.053 \text{ calories.}$$

Per 1° difference:

$$0.053 \div 147 = 0.00036 \quad "$$

Conductance, in C. G. S. units:

$$0.00036 \times 3 = 0.00108$$

Remarks: This conductance calculates out 2.5 times as great as from the data on the heating-up period, the reason of the higher value being that the charge is at nearly uniform temperature during this reduction period, and therefore the difference between the temperature taken in the middle of the charge and the true temperature of the inner walls of the retort is less than before, and the error from this source less. If we make the same assumption as in the correction to the previous problem, *i.e.*, take the conductance of the retort material as 0.0030, the difference in temperature of the outer and inner walls of the retort during this period would calculate out

$$\frac{147 \times 0.00108}{0.0030} = 53°$$

while the center of the charge was then $147 - 53 = 94°$ cooler, on an average, than the inner wall of the retort from which it was deriving its heat.

These figures appear reasonable, and the writer would con-

clude, from the data so far available, that the conductance 0.003 probably represents a good approximation to the correct value for zinc retort material, but that, in order to use it, we should have more experimental data as to the average difference between the temperature of the inner walls of the retort and the temperature of the charge at various points in the retort.

Problem 133.

A zinc ore containing 50 per cent of zinc is mixed with 40 per cent of its weight of small anthracite coal, and retorted in a Belgian furnace. The recovery of zinc was 82 per cent of the zinc content of the ore. The consumption of anthracite to heat the furnace was 2.25 tons per 10 of ore. The anthracite contained 90 per cent of carbon and 10 per cent of ash, and had a calorific power of 7500.

Required:

(1) The total consumption of fuel per 1000 of zinc obtained.

(2) The efficiency of transfer of heat from the furnace gases to the charge.

Solution:

(1) Zinc charged, per 1000 of zinc obtained

$$1000 \div 0.82 = 1220$$

Ore charged, per 1000 of zinc obtained

$$1220 \div 0.50 = 2440$$

Coal charged with ore

$$2440 \times 0.40 = 976$$

Coal burned on grate

$$2440 \times 2.25 = 5490$$

Total coal used, per 1000 of zinc obtained

$$976 + 5490 = 6466 \qquad (1)$$

(2) Calorific power of coal burned

$$5490 \times 7500 = 41{,}170{,}000$$

Heat required to raise ore to reduction point

$$2440 \times 159 = 387{,}960$$

Heat required to raise fuel to reduction point

Ash	98×159	= 15,580
Carbon	878×396	= 347,690

Total to raise charge to reduction point

= 751,230

Heat absorbed in distilling away 1000 of zinc

= 1,269,000

Total heat utilized

= 2,020,230

Thermal efficiency of utilization of the fuel

$$\frac{2,020,230}{41,170,000} = 0.049 = 4.9 \text{ per cent.} \qquad (2)$$

Problem 134.

Natural gas from Iola, Kan., has the following composition:

CH^4	93	per cent.
H^2	2	"
CO	1	"
C^2H^4	1	"
N^2	3	"

It is used in a zinc retort furnace, at an efficiency of transfer of heat to the charge of 4.9 per cent, as calculated in Prob. 133, working a charge which absorbed 2,000,000 Calories per 1000 kilograms of zinc distilled off.

Required: The volume of natural gas required to be used to displace the anthracite fuel used per 1000 kilograms of zinc produced. The cubic feet of gas per 1000 lbs. of zinc produced.

Solution:

Calorific power of the gas

CH^4	0.93×8623	=	8009
H^2	0.02×29030	=	581
C^2H^4	0.01×14365	=	144
CO	0.01×3062	=	31
			8765

This result may be called Calories per cubic meter of gas, or ounce-calories (1° C.) per cubic foot according to whether it is desired to work in metric units or the English system.

Cubic meters of gas required, per 1000 kilograms of zinc produced:

$$\frac{2{,}000{,}000}{0.049} \div 8765 = \mathbf{4{,}700} \text{ cubic meters.}$$

Per 1000 lbs. of zinc produced:

$$\frac{2{,}000{,}000}{0.049} \times 16 \div 8765 = \mathbf{75{,}200} \text{ cubic feet.}$$

Electric Smelting of Zinc Ores.

In an interesting communication to the *American Electrochemical Society* (Vol. XII, p. 117), Gustave Gin calculates the electric power necessary for the smelting of several varieties of zinc ore, assuming that the zinc vapor and other gases pass out of the furnace at the usual high temperature—1200° C.

Mr. Gin makes his calculations of heat required on the basis of molecular weight of zinc compound reduced; that is, for 81 parts of ZnO and 65 parts of Zn. Calculating to 1200°, he finds the heat in the products Zn and CO to be

In 65 parts Zn	26,720 Cal.
" 28 " CO	8,280 "
Sum	35,000 Cal.

whereas we calculate for the same quantities

In 65 parts Zn	37,695 Cal.
" 28 " CO	8,945 "
	46,640 Cal.

The difference between these numbers is principally in the latent heat of vaporization of zinc, which Gin assumes as 15,370 Calories, but which by a method of evaluation used by the writer figures out 27,670 Calories, and almost exactly the same value has been obtained by a different method by W. McA. Johnson.

Assume then, that we start with cold materials and end with

the products of the reaction leaving the retort at 1200°, the sum total of usefully applied heat is the heat of the reaction calculated at ordinary temperature plus the sensible heat of the products at 1200°, or

Heat absorbed by reaction, ordinary temperature	84,800 Cal.
Heat in necessary products, at 1200°	46,640
Total	131,440 "

To this must be added the sensible heat in the residue left in the retort, to get the total heat which has been applied to the charge. If the charge were pure ZnO, with the theoretical amount of carbon, the residue would be *nil*, but in practice there is always a residue of gangue with unused carbon.

Mr. Gin, having calculated the heat requirement on the above basis, then makes his calculations of power required per ton of ore smelted in the following ingenious way: The weight of each component of 1000 kg. of ore is divided by its molecular weight, and thus the number of molecular weights of material in one ton of ore determined, which, so to speak, gives a kind of chemical formula for the ore. An example will make this clear.

Composition of a calcined calamine zinc ore:

ZnO	40.50 per cent.
$ZnSiO^3$	38.07 "
Fe^2O^3	9.60 "
Al^2SiO^5	8.10 "
CaO	2.80 "

If we divide the weight of each compound present by its molecular weight we get the relative number of molecules present in the ore, and the formula for the ore:

	KG. IN 1000 KG.			
ZnO	405	÷ 81	= 5.0	molecular weights.
$ZnSiO^3$	380.7	÷141	= 2.7	"
Fe^2O^3	96.	÷140	= 0.6	"
Al^2SiO^5	81	÷162	= 0.5	"
CaO	28	÷ 56	= 0.1	"

The ore may therefore be represented by the formula

$5ZnO + 2.7ZnSiO^3 + 0.6Fe^2O^3 + 0.5Al^2SiO^5 + 0.1CaO.$

Assuming that the Fe^2O^3 becomes $FeSiO^3$, and that there is to be added enough CaO to form $CaSiO^3$ with the rest of the SiO^2 of the zinc silicate, we will need 1.5 CaO to do it, and since there is 0.1 CaO present, 1.4 CaO must be added, which represents $1.4 \times 56 = 79$ kg. of CaO. To form CO with the oxygen combined with the zinc and iron, reducing the latter to FeO, will require:

for 5	ZnO	5.0 C.
" 2.7	$ZnSiO^3$	2.7 "
" 0.6	Fe^2O^3	0.6 "
		Sum 8.3 C. = 100 kg.

If we use twice the theoretical amount of carbon needed for reduction we have the following balance sheets; weight in kilograms being enclosed:

ORE		ADDED		CHARGE	
5 ZnO	(405)	....		5 ZnO	(405)
2.7 $ZnSiO^3$	(381)	....		2.7 $ZnSiO^3$	(381)
0.6 Fe^2O^3	(96)	....		0.6 Fe^2O^3	(96)
0.5 Al^2SiO^5	(81)	....		0.5 Al^2SiO^5	(81)
0.1 CaO	(28)	1.4 CaO	(79)	1.5 CaO	(79)
		16.6 C	(200)	16.6 C	(200)

The distribution of this charge will be as follows:

CHARGE.		GASES.		RESIDUE.	
5 ZnO	(405)	5 Zn	(325)	....	
2.7 $ZnSiO^3$	(381)	2.7 Zn	(175)	....	
0.6 Fe^2O^3	(96)			1.2 $FeSiO^3$	(158)
0.5 Al^2SiO^5	(81)			0.5 Al^2SiO^5	(81)
1.5 CaO	(79)			1.5 $CaSiO^3$	(174)
16.6 C	(200)	8.3 CO	(232)	8.3 C	(100)

The essential reactions involved in the reduction are expressed by the reaction formula:

$$5ZnO + 2.7ZnSiO^3 + 0.6Fe^2O^3 + 1.5CaO + 8.3C = 7.7Zn + 1.2FeSiO^3 + 1.5CaSiO^3 + 8.3CO$$

The heat requirements per ton of ore treated may therefore be figured out as:

		Calories.
Decomposition of	$7.7ZnO = 84{,}800 \times 7.7$	= 652,960
"	$2.7ZnSiO^3$	
	into ZnO and $SiO^2 = 10{,}000 \times 2.7$	= 27,000
Decomposition of	$0.6Fe^2O^3$	
	into FeO and O $= 64{,}200 \times 0.6$	= 38,520
Heat absorbed in decompositions		= 718,480
Formation of	1.2 $FeSiO^3$	
	from FeO and $SiO^2 = 8{,}900 \times 1.2$	= 10,680
Formation of	1.5 $CaSiO^3$	
	from CaO and $SiO^2 = 17{,}850 \times 1.5$	= 26,770
Formation of	$8.3\ CO = 29{,}160 \times 8.3$	= 222,030
Heat evolved in formation heats		259,480
Net heat of chemical reactions absorbed		459,000
Sensible heat in	7.7 Zn $= 46{,}640 \times 7.7$	= 359,130
" "	8.3 CO $= 8{,}945 \times 8.3$	= 74,240
" "	8.3 C $= 5{,}760 \times 8.3$	= 47,810
" " slag	$\begin{cases} 1.2\ FeSi^1O^3 \\ 0.5\ Al^2SiO^5 \\ 1.5\ CaSiO^3 \end{cases}$	
	= 413 kilograms $= 460 \times 413$	= 200,000
Sensible heat in products and residue		= 681,180
Add heat absorbed in chemical reactions		= 459,000
Total heat requirement of the charge		= 1,140,180

Important principle: The heat absorbed in an electric furnace by chemical reactions is electric energy utilized at an efficiency of 100 per cent. It is only part of the sensible heat of the materials being treated which is lost by radiation and conduction. Heat losses by radiation and conduction in electric furnace processes should be expressed upon the total energy of the current *diminished by the heat absorbed in chemical reactions*, and not upon the total energy of the current. This principle has been expressed most clearly by Mr. F. T. Snyder,

of Chicago, the pioneer electric furnace zinc metallurgist of America.

Expressed thus, electric furnaces give higher efficiencies the greater the absorption of heat in chemical reactions taking place within them. In mere physical processes, such as melting, electric furnaces on a large scale give 75 per cent net efficiency, with 25 per cent loss by radiation and conduction. In the above case, figured out for 1000 kg. of zinc ore, 40 per cent of the total heat requirement is absorbed as chemical heat at 100 per cent efficiency, and 60 per cent is needed as sensible heat. This 60 per cent then represents the net sensible heating effect, and the loss of heat by radiation and conduction must be calculated as one-third of this quantity, and not one-third of the total net heat requirement. We therefore have:

	Calories.
Net heat requirements for chemical reactions.....	459,000
" " " " sensible heat.....	681,180
Loss by radiation and conduction.....	227,060
Gross heat requirement of the furnace.....	1,367,240

Kilowatt hours of current required

$$\frac{1,367,240}{860} = \mathbf{1530}$$

Mr. Gin's figures have been modified by the writer, as explained above, and anyone consulting his paper on this subject may make similar modifications to the other cases cited in that paper.

Mr. F. T. Snyder, of the Canada Zinc Company, at Vancouver, B. C., has operated the first practical electric zinc smelting furnace in America. Treating mixed lead and zinc ores, Mr. Snyder uses the furnace and process protected in his United States patents of July 2, 1907. (See *Electrochemical and Metallurgical Industry*, V. 323, 489.) The lead is obtained liquid, and the zinc also condensed to the liquid state before leaving the furnace proper, the heat of condensation being partly absorbed by water cooling the condensers and partly by the descending charges, which carry it back into the focus of the furnace. Under these circumstances, Mr. Snyder reports that he has attained unexpectedly low results as to

power requirement. It will be recalled, that in discussing the question of the electric smelting of zinc ores in general, and Mr. Gin's process in particular, we assumed the zinc vapor and CO gas to escape from the furnace at a minimum of 1033° C. If, as in Mr. Snyder's furnace, they escape at about 500°, the zinc liquid, the heat in these hot products is reduced very considerably, particularly that in the zinc. Mr. Snyder states in discussing Mr. Gin's paper (*loc. cit.*) that he has smelted pure zinc oxide at an expenditure of 1050 kilowatt hours per 1000 kilograms of oxide. Let us see how this coincides with the theoretical figures:

	Calories
Heat value of 1050 kw-hours.....	$= 1050 \times 860 = 903{,}000$
Heat of the chemical reactions, assumed to take place at ordinary temperatures.....	$1000 \times 687 = 687{,}000$
Sensible heat in products, at 500°	
Zinc: 800×80	$= 64{,}000$
CO: 342×152	$= 52{,}000$
	$= 116{,}000$
Leaving, by difference for radiation, conduction and cooling water	$= 100{,}000$

Mr. Snyder does not give details as to the exact working of his furnace, but his claim to reduce a ton of zinc ore with 1000 kw-hours is seen to be a possibility, if he can remove the zinc as liquid zinc from the furnace, not lose too much heat in cooling water, and get most of the heat of condensation of the zinc vapor usefully returned by the descending charges into the working focus of the furnace.

Snyder's furnace, working as claimed, would show a useful efficiency of

$$\frac{803{,}000}{903{,}000} = 0.88 = 88 \text{ per cent.}$$

on the current used, with 12 per cent losses. The real heat losses, however, should be expressed upon the energy used less that absorbed in chemical reactions, or as 100,000 loss on 216,000 used for sensible heat,

$$\frac{100{,}000}{216{,}000} = 0.46 = 46 \text{ per cent.}$$

This shows that the furnace loses by radiation, conduction and cooling water 46 per cent of the energy developed as sensible heat in the furnace, but the latter item is only 24 per cent of the total energy applied to the furnace.

In short, about three-quarters of all the energy consumed by the furnace is utilized in the heat of the chemical reactions produced; of the other one quarter, half of it is represented by the sensible heat of the products leaving the furnace and half is lost by radiation, conduction and cooling water.

Zinc Vapor.

The condensation of zinc from the state of vapor follows the same laws as regulate the condensing of all gases. If it is by itself in a cooler space, it condenses by contact with the walls as finely divided zinc dust (blue powder) if the walls are cold, as liquid zinc if the walls are hot, and it keeps on condensing until the tension of the remaining vapor is equal to the maximum tension of zinc vapor at the temperature of the condensing vessel. This condition having been reached, no more will condense until the condenser is cooled. At any temperature, therefore, an amount of zinc remains uncondensed corresponding to the maximum vapor tension of zinc at that temperature.

If other indifferent gases are present, the zinc vapor sustains only part of the atmospheric pressure, or pressure on the whole mixture, so that condensation cannot begin until a lower temperature is reached; that is, a temperature at which the maximum vapor tension of the zinc equals its partial vapor tension in the gas mixture. At this point condensation begins and continues as the temperature falls, the gas mixture always being saturated with zinc vapor. The phenomenon is precisely similar to the production of rain by the cooling of air containing moisture.

As to what the vapor tension of zinc is, the data are scanty. The boiling point under atmospheric pressure is 930° C., where its vapor tension is 760 mm. of mercury column. According to Barus, the maximum tension increases 6.67 mm. for each 1° C. increase of temperature. This is a difficult determination, but corresponds satisfactorily with the calculated increase from analogy to water and mercury.

Water, boiling at 100° C. (373° absolute), varies 1° in boiling

point for 27.20 mm. variation in vapor tension; mercury, boiling at 357° C. (630° absolute) varies 1° in boiling point for 12.66 mm. variation in vapor tension. The ratio of the two variations is seen to be somewhere in the inverse ratio of the two boiling points.

$$\frac{630}{373} = 1.7 \qquad \frac{27.20}{12.66} = 2.2$$

If we compare mercury with zinc, with the two boiling points 357° and 930° (630° and 1203° absolute), and the observed variations in vapor tension at the normal boiling point of 12.66 mm. and 6.67 mm. per 1° rise in boiling temperature, the two ratios are

$$\frac{1203}{630} = 1.91 \qquad \frac{12.66}{6.67} = 1.90$$

This coincidence justifies us completely in assuming that the vapor tension curve of zinc may be calculated directly from that of mercury, by assigning for any given vapor tension an absolute temperature to the zinc vapor of 1.91 times that of mercury vapor. For cadmium we may use the similar ratio of the normal boiling points in absolute degrees:

$$\frac{273+780}{273+357} = \frac{1053}{630} = 1.67$$

and thus calculate the cadmium curve from the mercury curve.

From incipient vaporization to ebullition in a vacuum.

Tension of vapor mm. of Hg.	Mercury C°.	Cadmium C°.	Zinc C°.
0.0002	0	183	248
0.0005	10	200	267
0.0013	20	216	286
0.0029	30	233	305
0.0063	40	250	324
0.013	50	267	344
0.026	60	283	363
0.050	70	300	382

Tension of vapor mm. of Hg.	Mercury C°.	Cadmium C°.	Zinc C°.
0.093	80	317	401
0.165	90	333	420
0.285	100	350	439
0.478	110	367	458
0.779	120	383	477
1.24	130	400	496
1.93	140	417	516
2.93	150	433	535
4.38	160	450	554
6.41	170	467	573
9.23	180	483	592

Before proceeding further, we would remark that cadmium melts at 320° and zinc at 419°; that both can, therefore, show vaporizing phenomena nearly 150° below their melting points. At 9 mm. tension, 180° C., mercury begins to show the phenomena of ebullition, and we would, therefore, expect cadmium to " simmer " at 483° and zinc at 592°. Neither of these observations has as yet been experimentally investigated, so far as the author knows.

From ebullition in vacuum to normal boiling point.

Tension of vapor mm. of Hg.	Mercury C°.	Cadmium C°.	Zinc C°.
9.23	180	483	592
14.84	190	500	611
19.90	200	517	630
26.35	210	533	649
34.70	220	550	668
45.35	230	567	687
58.82	240	584	706
75.75	250	600	726
96.73	260	617	745
123.	270	634	764
155.	280	650	783
195.	290	667	802
242.	300	684	821
300.	310	700	840

Tension of vapor mm. of Hg.	Mercury C°.	Cadmium C°.	Zinc C°.
369.	320	717	859
451.	330	734	878
548.	340	750	897
663.	350	767	915
760.	357	780	930

The above table contains the more important data for the actual condensation of zinc, cadmium and mercury vapors in practice. Thus, if a mixture of zinc or cadmium vapor with an equal volume of indifferent gas goes into a condenser, the partial pressure of the metallic vapor being in this case only half an atmosphere, or 380 mm., no metal will commence to condense until the temperature of the gases is reduced to 862° for zinc and 720° for cadmium. If mercury vapor from a roaster is mixed with 19 times its volume of other gas, so that it only forms 5 per cent of the mixture, its partial tension will be only 5 per cent of 760 mm. = 38 mm., and no mercury will commence to condense until the temperature of the gas mixture is reduced to 224°. These temperatures are exactly analogous to the phenomenon of the dew point of moist air, the temperature at which rain forms.

From normal boiling point to high pressures.

Tension of vapor atmospheres.	Mercury C°.	Cadmium C°.	Zinc C°.
1.0	357	780	930
2.1	400	851	1012
4.25	450	934	1107
8.	500	1018	1203
13.8	550	1101	1298
22.3	600	1185	1394
34.0	650	1268	1489
50.	700	1352	1585
72.	750	1435	1680
102.	800	1519	1776
137.5	850	1602	1871
162.	880	1652	1928

The latter table may have several special applications. If zinc, for instance, were placed in a closed electric furnace filled with indifferent gas and capable of supporting 100 atmospheres pressure, zinc could be kept in the liquid state up to some 1700° C., and its alloying with other metals greatly facilitated. In the making of brass, for instance, much zinc is lost by volatilization at the melting point of the copper used, yet a pressure on the furnace of four atmospheres would entirely prevent loss of zinc at the melting point of copper. Induction electric furnaces could easily be run inside a pressure vessel at this temperature, and the pressure be relieved gradually as the temperature of the melted alloy was reduced. To keep zinc from boiling, or to keep it in the liquid state, at 1300°, not a high temperature, would require a pressure of nearly 14 atmospheres to prevent it from boiling *ad libitum*.

Problem 135.

Roasted zinc sulphide ore, consisting practically of pure ZnO, is reduced by carbon, and the reduction gases passed into a condenser. Assume the reaction to be

$$ZnO + C = Zn + CO.$$

Required:

(1) The temperature at which zinc commences to condense from the above gas mixture.

(2) The proportion of the zinc condensed out for each 1° reduction of temperature below this " dew point."

(3) The proportion of the zinc escaping uncondensed, if the gas escapes from the condenser at 600° C.

(4) How would these data be affected, if the reduction was taking place at Denver, 1500 meters above sea level, barometer 560 mm?

Solution:

(1) Since zinc vapor has been shown to have a specific gravity of 32.5 referred to hydrogen gas at the same temperature and pressure, and the molecular weight of hydrogen gas, formula H^2, is 2, the molecular weight of zinc vapor must be $2 \times 32.5 = 65$. This coincides with the atomic weight of zinc, and therefore zinc vapor is monatomic and the symbol of its molecule is Zn. The gas mixture in the above equation con-

tains, therefore, one molecule each of its constituents, and, therefore, each gas supports half the atmospheric pressure. This is ordinarily expressed by saying that the gas is half one constituent and half the other, meaning that if the two gases were separated and each measured under the prevailing normal pressure, the volume of each would be half the volume of the gas mixture. The statement that each supports half the normal pressure is the more scientific and logical, for in a gas mixture each gas certainly possesses the volume of the mixture, but under only a fraction of the pressure on the mixture, said fraction being identical with the fraction of the volume of the whole which it would constitute, if measured separately under the pressure supported by the mixture.

Consulting the table, we find zinc vapor to have a pressure of 380 mm. at **862°**. This would, therefore, be the dew point, at which the zinc would commence to condense. (1)

(2) At this condensing temperature, a difference of 19° in the temperature corresponds to 82 mm. difference in the maximum vapor tension, and, therefore, in this gas mixture at this temperature, a reduction of 1° in its temperature will reduce the tension of the zinc vapor $82 \div 19 = 4.3$, or practically 4 mm. This will result in the condensation of $\frac{4}{380}$ th. of the zinc, because its tension was 380 and was reduced to 376, and, therefore, $\frac{376}{380}$ th. of it remained uncondensed. The proportion condensed for the reduction of 1° in temperature is, therefore, a trifle over **1** per cent. (2)

(3) Leaving the condenser at 600°, the tension of the zinc vapor escaping would be, from the table, 11.6 mm. The tension of the CO gas would, therefore, be $760 - 11.6 = 748.4$ mm. For every cubic meter of mixed gases, at 862°, containing a cubic meter of zinc vapor at that temperature and 380 mm. pressure, there will escape a fraction of a cubic meter of mixed gas at 600°, containing zinc vapor at 11.6 mm. pressure. The fractional volume can be calculated from the tension on the CO.

1 m^3 CO at 862° and 380 mm. pressure, reduced to 600° and 748.4 mm. pressure, becomes

$$1 \times \frac{600+273}{862+273} \times \frac{380}{748.4} = 0.381 \text{ m}^3.$$

This is, then, the actual volume of gas mixture escaping, for each actual 1 m^3 of gas mixture in the condenser at the " dew point," 862°.

The uncondensed zinc vapor is, therefore, 0.381 m^3 at 600° and 11.6 mm. tension. This would be, at 862° and 380 mm. tension

$$0.381 \times \frac{862+273}{600+273} \times \frac{11.6}{380} = 0.015 \text{ m}^3.$$

There, therefore, escaped uncondensed

$$\frac{0.015}{1.000} = 0.015 = \mathbf{1.5} \text{ per cent of the zinc.} \qquad (3)$$

A quicker solution, not so easy to understand, however, is

$$\frac{11.6}{748.4} = 0.015 = \mathbf{1.5} \text{ per cent uncondensed.}$$

(4) If the operation takes place at such elevation above sea-level that the barometer stands normally at 560 mm., then the partial pressure of the zinc vapor in above case would be 280 mm. instead of 380 mm. and the " dew point " or temperature at which condensation commences would be 835° instead of 862°, as under previous conditions.

At this temperature, a difference of 1° in the temperature corresponds to a difference of 3 mm. in the tension of the zinc vapor, producing therefore a condensation of the zinc present, per 1° fall of temperature, of $3 \div 280 = 0.011 = 1.1$ per cent, instead of 1.2 per cent.

If the temperature of the escaping gases is 600°, with the saturated zinc vapor at 11.8 mm. tension and the carbonous oxide, CO, at $560 - 11.8 = 548.2$ mm., the proportion of the original quantity of zinc escaping uncondensed is $11.8 \div 548.2 = 0.022 = 2.2$ per cent, instead of 1.5 per cent.

Condensation of Zinc and Mercury Vapors.

The temperature at which a metallic vapor, like zinc or mercury, commences to condense, depends upon the vapor tension curve of the metal and the amount of other uncondensable gas

with which it is mixed. These intermixed gases reduce the pressure upon the metallic vapor, and lower the temperature at which the vapor becomes saturated vapor. The phenomenon is exactly analogous to the " dew point " of air and the precipitation of rain.

Problem 136.

A roasted zinc ore contains 15 per cent. $Fe^2 O^3$ and 70 per cent. Zn O. It is reduced by excess of carbon, in a retort.

Required:

(1) The average composition, by volume, of the gas mixture entering the condenser, assuming no CO^2 in it.

(2) The " dew point " of the mixture at which it begins to deposit zinc.

(3) The percentage of zinc escaping condensation, if the gases leave the condenser at 600° C.

Solution:

(1) Per kilogram of zinc there is used, assuming complete reduction:

$$1 \div (0.70 \times 65/81) = 1.78 \text{ kg.}$$

Oxygen in 1.78 kg. of ore:

$$\text{As Zn O} = 1 \times 16/65 = 0.246 \text{ kg.}$$
$$\text{As } Fe^2O^3 = 1.78 \times 0.15 \times 48/160 = 0.080 \text{ "}$$
$$\text{Sum} = 0.326 \text{ "}$$

$$\text{Co formed} = 0.326 \times 28/16 = 0.57 \text{ "}$$
$$\text{Volume of CO} = 0.57 \div 1.26 = 0.45 \text{ m}^3$$
$$\text{Volume of Zn} = 1.00 \div 2.93 = 0.34 \text{ m}^3$$

$$\text{Sum} = 0.79 \text{ m}^3$$

Percentage composition of gases:

$$\text{CO} = 57 \text{ per cent.}$$
$$\text{Zn} = 43 \text{ "} \qquad (1)$$

(2) If the barometric pressure is assumed normal, then the zinc vapor supports

$$760 \times 0.43 = 327 \text{ mm}$$

and the temperature at which the mixture becomes saturated with zinc vapor is found from the table on page 620 to be **847°**.

This is 83° below the normal boiling point of zinc.

(3) From 847° down, the vapor in the retort will be always saturated, its tension being found from the tables. The proportion of original zinc condensed, or remaining uncondensed, cannot be inferred simply from the vapor tension at any temperature. For instance, the vapor tension of the zinc at 600° C. is 12 mm of mercury column. The CO gas leaving the condenser at this temperature will, therefore, be at a tension of 760—12 = 748 mm, and will be accompanied by 12/748 of its volume of zinc vapor; as it came into the condenser it was accompanied by 327/433 of its volume of zinc vapor. The ratio of these two quantities or proportions represents the real fraction of the zinc escaping uncondensed; that is, the proportion escaping condensation, in terms of the total zinc concerned, is

$$12/748 \div 327/423 = 0.016 \div 0.773 = 0.008 = 0.8 \text{ per cent.}$$

The same result can be calculated in several ways. One is based on the datum that at any given temperature zinc vapor is $65 \div 28 = 2.3$ times as heavy as CO gas.

Problem 137.

Numerous attempts have been made to reduce Zn O continuously in a blast furnace, and condense the zinc from the gases. In such a case, the gases will consist of zinc vapor, carbon monoxide and nitrogen, and the deficit of reduction heat must be obtained by the burning of carbon to CO at the region of the tuyeres. A low charge column must be used in order that the gases pass out hot enough to carry the zinc. Assume the gases to escape at 900° C., and the furnace to lose by radiation and conduction, etc., an amount of heat equal to the sensible heat in the blast used.

Required:

(1) The amount of fixed carbon to be charged into the furnace, per 2000 lb. of zinc.

(2) The composition of the gases leaving the furnace.

(3) The temperature at which these gases will begin to deposit zinc or become saturated with zinc vapor.

(4) The proportion of the zinc they carry which will escape from the condensers, as vapor, at 600° C.

(5) The pressure necessary to apply to the furnace to keep

the zinc in the melted state at the minimum temperature of reduction, 1033° C.

Solution:

(1) If the reaction is assumed as practically

$$Zn\,O + C = Zn + CO$$

there is needed for reduction, per 2000 lb. of zinc

$$2000 \times (12/65) = 369 \text{ lb.}$$

There is in this reaction a deficit of heat, which is per 65 parts of zinc concerned simply

$$(Zn, O) - (C, O) = 84{,}800 - 29{,}160 = 55{,}640.$$

This deficit can only be made up by burning more C to CO right at the tuyeres. If two more atoms of carbon were burned we would have a little more than enough heat. We will, therefore, assume the reaction at the tuyere region as the using of one atom of carbon for reduction and of double as much for supplying the heat deficit, and since one volume of oxygen is accompanied by 3.81 volumes of nitrogen, the whole reaction will be

$$Zn\,O + 3\,C + O^2 + 3.81\,N^2 = Zn + 3\,CO + 3.81\,N^2.$$

The amount of fixed carbon necessary is approximately three times that necessary for reduction only and amounts, per 2000 lb. of zinc, to

$$36 \times \frac{2000}{65} = \mathbf{1108} \text{ lb.} \qquad (1)$$

(2) The furnace gases, therefore, contain, by volume,

Zinc vapor	= 1	volume	= **12.8**	per cent.
Carbon monoxide	= 3	"	= **38.4**	"
Nitrogen	= 3.81	"	= **48.8**	" (2)

(3) The gases will be saturated with zinc vapor when the partial pressure of the zinc, which is

$$760 \times 0.128 = 97 \text{ mm}$$

is equal to the maximum tension of zinc at the temperature attained. This is at **745**° C., as seen from inspecting the vapor tension tables, or 185° below the normal boiling point of zinc. (3)

(4) The relative volume of zinc vapor to uncondensable gas in the original gases is

$$\frac{12.8}{87.2} = 0.147$$

In the gases issuing from the condenser at 600° it would be

$$\frac{12.0}{748} = 0.016$$

The proportion of the zinc escaping condensation under these conditions would, therefore, be

$$\frac{0.016}{0.147} = 0.109 = \mathbf{10.9} \text{ per cent.} \qquad (4)$$

By cooling the gases to the melting point of zinc, it would be possible to leave uncondensed only

$$\frac{0.165}{759.8} \div 0.147 = 0.0014 = 0.14 \text{ per cent.}$$

(5) If it was a question only of keeping pure zinc from vaporizing at 1033°, in the absence of other gases, we could at once consult the vapor tension table, and find 2.2 atmospheres as the actual tension of zinc vapor at 1033°, corresponding to 1.2 atmospheres effective pressure upon the furnace. But in the gas mixture coming from the furnace the zinc is practically one-eighth, by volume, of the gases, which means that it sustains one-eighth of the pressure upon the whole. It would, therefore, take a tension of

$$2.2 \times 8 = 17.6 \text{ atmospheres}$$

to keep all this zinc in the liquid state, corresponding to an effective pressure of **16.6** atmospheres. (5)

This is an entirely impracticable working condition and shows the practical impossibility of the schemes upon which much money have been spent for reducing zinc ore to liquid zinc in a blast furnace run under high pressure.

Problem 138.

In the metallurgy of mercury, the average ore contains 2 per cent. of Hg S and is roasted by the use of 10 per cent. of its

weight of wood having an average composition of water 20 per cent., carbon 32, hydrogen 5.3, oxygen 42.7. Assume that just enough air enters to completely burn the sulphur and carbon, that the ore and air used are dry.

Required:

(1) The percentage composition by volume of the roaster gases.

(2) The temperature at which the mercury will commence to condense.

(3) The proportion of the mercury present escaping as vapor if the gases pass out of the condensers at 100° C., at 50° C., at 15° C.

Solution:

(1) Per 1000 kg. of ore, containing 20 kg. of Hg S, there must be burned

$$20\times32/232 = 2.8 \text{ kg of sulphur.}$$
$$100\times0.32 = 32 \text{ " " carbon.}$$

requiring of oxygen:

$$2.8\times1 = 2.8 \text{ kg.}$$
$$32 \times32/12 = 85.3 \text{ "}$$
$$\text{Sum} = 88.1 \text{ "}$$
$$\text{Nitrogen accompanying} = 293.7 \text{ "}$$
$$\text{Air} = 381.8 \text{ "}$$

Composition of the gases:

Hg =	17.2 kg =	17.2 ÷ 9.00 =	1.91 m^3 =	0.5	per cent.
SO^2 =	5.6 " =	5.6 ÷ 2.88 =	1.91 " =	0.5	"
H^2O =	68.0 " =	68.0 ÷ 0.81 =	83.95 " =	22.1	"
N^2 =	293.7 " =	293.7 ÷ 1.26 =	233.10 " =	61.3	"
CO^2 =	117.3 " =	117.3 ÷ 1.98 =	59.24 " =	15.6	"
			380.11 " =	100.00	(1)

(2) In reality, each of these gases possesses the volume of the gas mixture, and is at the above percentage of the normal barometric pressure upon the mixture. The tensions of the different constituents of the mixture are, therefore,

Hg	$760 \times 0.005 =$	3.8 mm
SO^2	$760 \times 0.005 =$	3.8 "
H^2O	$760 \times 0.221 =$	168.0 "
N^2	$760 \times 0.613 =$	465.9 "
CO^2	$760 \times 0.156 =$	118.5 "
		760. "

The mercury will, therefore, commence to condense when the temperature of the gas mixture is that of mercury vapor at a maximum tension of 3.80 mm. From the vapor tension table of mercury we find this to be 156° C., or 201° below the normal boiling point of mercury. Above this temperature the gas mixture is not saturated with Hg vapor and no condensation can occur. (2)

(3) In the gas mixture, the mercury vapor is equivalent to 3.8/760 of the volume of the whole, or 3.8/756.2 of the volume of the other gases. This latter proportion is 0.00503. At 100° C., the uncondensed mercury vapor can have a tension of 0.285 mm, leaving 759.715 to the other gases, and giving the ratio of mercury vapor to other gases 0.000375. Since the other gases have remained constant in amount, the proportion of mercury remaining condensed is

$$0.000375 \div 0.00503 = 0.075 = 7.5 \text{ per cent.}$$

If the temperature of the mixture is reduced to 50° C., the mercury vapor remaining can exert a tension of only 0.013 mm and the water vapor only 92 mm. The other gases present will therefore sustain 760— (92+0.013) = 668 mm. In the original mixture the Hg and H^2O vapors are, respectively, equivalent to

Hg	$3.8 \div 587.2 = 0.0065$
H^2O	$168.0 \div 587.2 = 0.2860$

of the volume of N^2, CO^2 and SO^2 together.

In the gas escaping at 50° the Hg and H^2O will be equivalent to

Hg	$0.013 \div 668 = 0.00002$
H^2O	$92. \div 668 = 0.1377$

of the volume of the same gases.

The proportions of the Hg and H^2O escaping uncondensed at 50° will, therefore, be

$$\text{Hg} \quad 0.00002 \div 0.0065 = 0.0031 = 0.31 \text{ per cent.}$$
$$H^2O \quad 0.1377 \div 0.2860 = 0.4815 = 48.15 \text{ per cent.}$$

By exactly similar reasoning, using the maximum tensions of Hg and H^2O at 15° (0.0009 mm and 13 mm, respectively), the proportions of each to the $N^2 + CO^2 + SO^2$ are

$$\text{Hg} \quad 0.0009 \div 747 = 0.0000012$$
$$H^2O \ 13. \quad \div 747 = 0.0174$$

and the proportions escaping condensation would be

$$\text{Hg} \quad 0.0000012 \div 0.0065 = 0.00018 = 0.018 \text{ per cent.}$$
$$H^2O \ 0.0174 \quad \div 0.2860 = 0.06064 = 6.064 \text{ per cent.} \quad (4)$$

The differences between these percentages and 100 will be the proportions of these materials condensed to the liquid state.

Metallic Mist or Fume.

When zinc or mercury are in the state of vapor their atoms are each separate from other atoms. Chemically speaking, their vapor molecules are mon-atomic. On condensing to the liquid state we do not know whether the atoms come together into compound molecules or whether they simply come closer together. In either case, the molecules of the liquid metal, as the temperature is reduced low enough to form them, exist at first as isolated molecules, constituting the liquid metal in its finest possible state of sub-division, so small that it is for the time being practically still a gas. If, however, we give these liquid molecules the possibility of uniting to liquid masses, we get the latter. This is a matter principally of reducing the surface tension which holds the liquid molecules each to itself as a sphere. Contact with a rubbing surface, with dust particles, filtration through cloth, or even electrification (perhaps a magnetic field) reduce this surface tension and cause agglomeration into liquid masses which precipitate.

The amount of liquid or solid particles thus held in suspension and escaping with the current of uncondensable gas is entirely independent of the quantity escaping as true vapor, which has been calculated above, except in so far as they are both functions of the amount of said uncondensable gas. The velocity of the escaping current is a large factor in the amount of mist, because the carrying power of gas for mist particles varies

probably with the cube of its velocity, so that halving the velocity of the issuing gas will diminish greatly this source of loss. Large settling chambers in which the mist can deposit, because of stagnation of the gas current, and large rubbing surfaces, are effective means for catching or depositing the mist. Filtration through bags is still more effective.

In the case of zinc, the solidifying point is 420°, while condensation from the state of vapor begins at, say, 860°. In this interval only can the condensed particles, as a mist, collect together to liquid zinc. If the temperature passes quickly through this range, the particles have little chance to agglomerate into liquid masses, and the proportion which chills into solidified mist particles is increased. These solidified mist particles, analogous to " hoar frost " in nature, form the well known " blue powder " of the zinc works. It settles in large settling chambers, and is in extremely fine particles, mostly under 0.01 mm in size. It is quite easy to collect all the zinc in this form if the vapor is chilled suddenly and the resulting gas settled properly or filtered.

The loss of mercury or zinc as mist or hoar frost is therefore, to be considered entirely apart from the loss as true vapor; it may be smaller than the latter and it may be larger; its amount varies particularly with the nature of the settling apparatus and the velocity of the gases as they escape. The theory as to its amount under any given set of conditions would be very difficult to elaborate, and the data for doing so with exactness are practically unknown. The best that can be done at present is to study the loss as mist or hoar frost in actual practice, experimentally, and tabulate the actual results as a guide for future metallurgical use.

CHAPTER V.

METALLURGY OF ALUMINIUM.

The two essential principles here involved are "differential reduction" as used in the electric furnace purification of alumina, and "electrolytic furnace operation," as illustrated in the decomposition of the alumina by electrolysis in the manner usually practiced. Only the latter problem will be covered here.

Electrolytic Furnace Reduction of Alumina.

The Hall process is beautifully simple and technically admirable. $Al^2 O^3$ is found to dissolve in melted alkaline-aluminium double fluorides; it is as pretty a case of solution, so far as appearances go, as dissolving a spoonful of powdered sugar in a glass of distilled water. The melting point of the fused fluorides is reduced by the solution of alumina, just as that of water is reduced by dissolving salt. In passing the electric current the constituents of the dissolved alumina appear at the electrodes, oxygen at the anode and aluminium at the cathode. The best practical arrangement is to use a carbon-lined pot, with molten aluminium in the bottom as the cathode, upon it a few inches depth of the bath, and dipping into this the carbon anodes. The writer has given most of the technical details of this operation in his treatise on "Aluminium," and Prof. Haber has published extensive laboratory studies of the process in the *Zeitschrift für Elektrochemie.*

With a solvent salt consisting of melted sodium fluoride and aluminium fluoride, such as called for in one of the Hall patents, with alumina dissolved therein, and using carbon anodes, the electrolytic elements of the process are simplicity itself. The bath contains sodium, aluminium, fluorine and oxygen, and the anode is carbon. Under these conditions those elements or compounds will form at the electrodes which cannot further react upon the bath material; in other words, those materials most stable in contact with the bath material or electrodes. A mo-

ment's reflection explains what happens, and what must happen. At the cathode, sodium cannot be liberated because metallic sodium reacts chemically on this bath, separating out aluminium; therefore, the electrolytic reducing tendency at the surface of the cathode can only expend itself in separating out aluminium. At the anode, fluorine cannot be liberated because fluorine acts strongly upon alumina even when cold, converting it into fluoride and expelling its oxygen; therefore, the electrolytic perducing tendency at the surface of the anode will tend to set free oxygen. But oxygen cannot be set free at a carbon surface at a cherry-red heat because of its inevitable tendency to unite with the carbon to form CO. The electrolytic agency at the surface of the carbon anode must, therefore, cause the formation of CO. The whole electrolytic operation results in the removal of Al^2O^3 from the bath and the formation of aluminium and carbon monoxide.

The thermochemical relations, as far as known, agree absolutely with the above explained experimental results. The materials in presence of each other are sodium fluoride, aluminium fluoride, aluminium oxide and carbon. The heats of formation of these, per molecule and per chemical equivalent concerned, are as follows:

(Na, F)	= 109,720	= 109,720	per chemical equivalent.
(Al, F^3)	= 275,220	= 91,740	" " "
(Al^2, O^3)	= 392,600	= 65,430	" " "
(C, O)	= 29,160	= 14,580	" " "

The heat of formation of carbon tetra-fluoride is unknown, but is probably small, since it is so difficult to form.

From the last column, which largely governs the work done by the current, we see that the current does far the least work when it decomposes alumina; in fact, it does still less, by 14,580 calories, because of the assistance rendered by carbon uniting with the oxygen. Now, although the electrical current does not consistently adhere to the doctrine of " least work," yet it does in this case because forced to do so by the chemical relations of sodium, aluminium, fluorine, oxygen and carbon at the temperature of the bath, as explained in the preceding analysis. It is probable that in electrolysis the chemical relations of the possible products control what the current does rather than the

thermochemical relations alone, but in most cases the two conditions or controlling circumstances coincide in their influence and lead to identical results. This is the case in the process in question; it is absolutely normal and is explainable by either method of reasoning.

If the operation is run with a small vessel and correspondingly small current, the heat necessarily evolved by the passage of the current is small compared to the conduction and radiation losses and must be supplemented by outside heating to keep the contents at proper temperature. If the size of the operation is increased in all its items and dimensions, the necessarily generated internal " resistance " heat will suffice to keep the bath at the requisite temperature, when the enlargement is done on a certain scale. If enlarged past this point, too much internal heat is unavoidably generated and means must be used to artificially cool the pot.

Problem 139.

An electrolytic vessel is composed of a block of carbon 25 cm cube, with a cavity 10 cm square by 10 cm deep inside. The cavity has a round carbon, 5 cm diameter, dipping into it. The vessel weighs 30 kilograms; the fused bath in the cavity 2 kg; the carbon immersed in it 0.1 kg. The specific heat of the carbon is 0.5, of the bath 0.3, at the running temperature. An experiment showed that the bath material cooled off, at the working temperature, at the rate of 10° C. per minute, the walls of the vessel at an average rate of 2° C. per minute, when left to cool by themselves.

Required:

(1) The number of watts which must be converted into heat in the vessel in order to maintain it at the working temperature.

(2) Assuming 75 per cent. of the theoretical ampere efficiency to be obtained, what amperes passed through the pot will keep it at working temperature if the working voltage is kept at 10 volts?

Solution:

(1) The 30 kg of vessel material losing heat at the rate of 2° per minute, with specific heat of 0.5, gives a heat loss per minute of

$$30 \times 0.5 \times 2 = 30 \text{ Calories.}$$

Similarly, the immersed carbon in the cavity and the bath material itself lose

$$0.1 \times 0.5 \times 10 = 0.5 \text{ Calories.}$$
$$2.0 \times 0.3 \times 10 = 6.0 \quad \text{“}$$

The total heat loss is, therefore, 36.5 Calories per minute.

To maintain the temperature constant the current must furnish this heat, and since 1 watt is 0.239 gram calories per second, the watt energy thus converted into heat must be

$$\frac{36.5 \times 1000}{0.239 \times 60} = \mathbf{2545} \text{ watts} \qquad (1)$$

(2) If all the amperes passing through separated out metal the voltage absorbed in decomposition in the bath would be from the thermochemical heats of formation of chemical equivalent quantities of $Al^2 O^3$ and CO:

$$\frac{65{,}430 - 14{,}580}{23{,}040} = 2.2 \text{ volts.}$$

If 75 per cent. of the amperes are efficient, the voltage thus absorbed is

$$2.2 \times 0.75 = 1.65 \text{ volts.}$$

The voltage disappearing in overcoming ohmic resistance will then be

$$10 - 1.65 = 8.35 \text{ volts}$$

and the current which when passed will keep the pot at working temperature will be

$$\frac{2545}{8.35} = \mathbf{305} \text{ amperes.} \qquad (2)$$

The above-used principles are applicable to any kind of electrolytic-furnace operation.

INDEX.

ADDICKS, L., on energy loss at electrical contacts 562
Air, composition of 4
Air, received by converter 336
Air, required by converter 333
Alloys, heats of formation 37
Alloys, thermophysics of 109
Alumina, action in blast furnace slag 256
Alumina, behavior in the blast furnace 240
Alumina, reduction of 658
Alumina, thermophysics of 123
Aluminates, heats of formation of 35
Aluminium alloys, thermophysics of 113
Aluminium compounds, heats of formation of 18, 37
Aluminium compounds, thermophysics of 139
Aluminium conductors, economical size of 570
Aluminium conductors, heating of, in use 572
Aluminium, electrical conductivity of 569
Aluminium, heat of oxidation of 353, 374
Aluminium, metallurgy of 658
Aluminium, reduction of lead oxide by 586
Aluminium, thermophysics of 80
Amalgam furnace, efficiency of 107
Amalgams, heats of formation of 37
Ammonia gas, mean specific heat of 142
Anode, insoluble, use of 551
Anode, soluble, use of iron as 548
Anode, use of matte as 539
Anthracite coal, combustion of 220, 221
Antimonides, heats of formation of 23
Antimonides, thermophysics of 136
Antimony alloys, thermophysics of 101
Antimony, behavior in the blast furnace 240
Antimony, compounds, heats of formation of 23
Antimony, thermophysics of 95
Aqueous vapor, maximum tension of 111
Argo, Col., reverberatory smelting at 501
Arsenic, behavior in the blast furnace 240
Arsenic compounds, heats of formation of 33
Arsenic compounds, thermophysics of 136, 138
Arsenic, thermophysics of 88
Arsenides, heats of formation of 23
Ashcroft's process for copper ores 537
Atacamite, formula of 537
Atomic weights 1

BALANCE sheet of blast furnace 235
Barium compounds, heats of formation of 18–40
Barium compounds, thermophysics of 113–144
Barium, thermophysics of 97
Bauxite, efficiency of furnace, in melting 127
Beeswax, thermophysics of 142
Belgian furnace, distillation of zinc ore in a 635
Bergfeld, on the boiling of silver and gold 615

Beryllium compounds, heats of formation of 18–40
Beryllium compounds, thermophysics of 113–144
Beryllium, thermophysics of 76
Bessemerizing copper matte 525
Bessemer process, problem concerning 11
Bessemer process, the 333
Betts' refining process for lead 598, 599, 602
Bi-carbonates, heats of formation of 29
Bismuth alloys, thermophysics of 110
Bismuth compounds, heats of formation of 18–40
Bismuth compounds, thermophysics of 113–144
Bismuth, thermophysics of 102
Bi-sulfates, heats of formation of 33
Bituminous coal, combustion of 219, 221, 222, 223, 226
Blast, amount used in blast furnace 244
Blast, dry, Gayley process of producing 330
Blast, dry, the rationale of 309
Blast engines, efficiency of 493, 590
Blast furnace, balance sheet of 235
Blast furnace, carbon needed in the 277
Blast furnace gas, in gas engines 226
Blast furnace gases, surplus power from 272
Blast furnace, heat balance sheet of 281
Blast furnace, reduction of zinc ores 651
Blast furnace, temperature in 223
Blast furnace, utilization of fuel in the 268
Blast, heating of, apparatus for 318
Blast, hot, the function of 308
Blast pressure required in Bessemer process 340
Blast, warm, use in pyritic smelting 487
Blast, work done in producing 313
Blister roasting of copper matte 523
Blowing engines, efficiency of 299
Boiling of metals in a vacuum 614
Boiling of zinc 641
Borates, heats of formation of 34
Boron compounds, heats of formation of 18–40
Boron compounds, thermophysics of 138
Boron, thermophysics of 77
Brass, thermophysics of 112
Bringing forward of copper matte 514
Bromides, thermophysics of 133
Bromine, thermophysics of 89
Bronze, thermophysics of 111
Bullion, gold, electrolytic refining of 606
Bullion, silver, electrolytic refining of 605
Burgess process of refining iron 446
Butte, Mont., copper concentrates from 479
Butte, Mont., roasting furnace at 482

Cadmium alloys, thermophysics of 113
Cadmium compounds, heats of formation of 18–40
Cadmium compounds, thermophysics of 131–144
Cadmium, thermophysics of 93
Cadmium, vapor tension of 644
Cæsium compounds, heats of formation of 18–40
Cæsium, thermophysics of 96
Calcium compounds, heats of formation of 18–40
Calcium compounds, thermophysics of 131–144
Calcium oxide, heat absorbed in reducing 293

Calcium oxide, thermophysics of 124
Calcium, thermophysics of 83
Calorific power of fuels, calculation of 503
Calorimeter, test for specific heat by 225
Calorimeter, test for temperature by 224
Campbell, H. H., furnace data by 393
Canada, electrical processes in 435
Canada Zinc Co., operations of the 641
Carbides, heats of formation of 25
Carbon, amount needed in the blast furnace 277
Carbon, heat of oxidation of 352, 375
Carbon, thermophysics of 77
Carbonates, heat absorbed in decomposing 291
Carbonates, heats of formation of 28
Carbonates, thermophysics of 137
Carbonic oxide, thermophysics of 122
Carbonous oxide, thermophysics of 121
Cathodes, use of copper matte as 545
Cathodes, use of lead sulfide as 598
Cement copper, composition of 548
Cerium compounds, heats of formation of 18, 40
Cerium, thermophysics of 97
Chalcopyrite, composition of 474
Charge, blast furnace, calculation of 250
Chimney draft 185
Chimney draft, problems concerning 192, 194, 224, 230, 231
Chimney for open-hearth furnace 395
Chlorates, thermophysics of 139
Chlorides, heats of formation of 27
Chlorides, thermophysics of 131
Chlorine, thermophysics of 82
Chromates, thermophysics of 138
Chromium, heat of oxidation of 353, 374
Chromium, thermophysics of 84
Coal, combustion of powdered 8
Cobalt, behavior in the blast furnace 240
Cobalt compounds, heats of formation of 18–40
Cobalt compounds, thermophysics of 131–144
Cobalt, thermophysics of 87
Coehn, improved Hoepfner apparatus 558
Coke-oven gases, combustion of 219–228
Coke, use of, in pyritic smelting 488
Columbium, thermophysics of 90
Compression of blast, work done in 313
Concentration of zinc ores, cost of 621
Condensation of metallic vapors 649, 654
Conduction of heat, principles of 200
Conductivity for heat, tables of 203, 211
Conductors, electrical, economic size of 564
Conductors, electrical, heating of, in use 568
Constants, thermochemical 38–40
Contacts, electric, energy loss at 562
Copper alloys, thermophysics of 111
Copper, behavior in the blast furnace 240
Copper, calculations on metallurgy of 469, 619
Copper chloride, electrolysis of 537, 557
Copper compounds, heats of formation of 18–40
Copper compounds, thermophysics of 131–144
Copper, electrical conductivity of 567
Copper, electrolytic refinery of 558

Copper matte, composition of....469, 471
Copper, principles of the metallurgy of.... 472
Copper ores, electric smelting of.... 572
Copper solutions, physical properties of.... 611
Copper solutions, resistivity of.... 559
Copper, thermophysics of.... 87
Crushing of zinc ores, cost of.... 621
Cupola, thermal efficiency of.... 115
Cyanates, heats of formation of.... 36
Cyanides, heats of formation of.... 35, 36
Cyanides, thermophysics of.... 136

Damour, on furnace efficiency....416, 423
Decomposition of moisture of blast.... 293
Dehydrating charges, heat absorbed in.... 290
Dellwick-Fleischer gas producer.... 179
Distillation of zinc from ore.... 632
Dried blast, rationale of action of.... 309
Dried blast, temperatures attained with.... 312
Drying air blast commercially.... 325
Drying charges, heat absorbed in.... 290
Drying of wet peat.... 227
Ducktown pyrrhotite, smelting of.... 489
Dulong and Petit's laws of specific heats.... 70
Dulong's laws of heat of combustion of coals.... 48

Efficiency of electric furnaces.... 640
Efficiency of electric heating.... 441
Efficiency of furnaces, discussion of.... 104
Efficiency of open-hearth furnaces.... 396
Eissler's hydrometallurgy of copper.... 469
Eldred process of combustion.... 55
Electric furnaces, efficiency of.... 640
Electric melting of steel.... 440
Electric reduction of iron ore.... 429
Electric refining of iron.... 446
Electric smelting of copper ores.... 572
Electric smelting of zinc ores.... 637
Electrical contacts, energy loss at.... 562
Electrolytic furnace, definition of.... 534
Electrolytic furnace for reducing aluminium.... 658
Electrolytic refining of copper.... 558
Electrolytic refining of gold.... 610
Electrolytic refining of iron.... 446
Electrolytic refining of lead.... 598
Electrolytic refining of silver.... 605
Electrolytic refining, principles of.... 536
Electrometallurgy of copper.... 534
Electrometallurgy of iron and steel.... 429
Electrometallurgy of lead.... 598
Electrothermal processes, definition of.... 535
Ely, Vermont, copper ore from.... 475
Ethylene, mean specific heat of.... 142
Evans-Klepetko furnace, calculations on.... 482

Feed-water heater, utility of.... 225
Ferro-cyanides, heats of formation of.... 36
Fire-clay, heat conductivity of.... 630
Flues, size of.... 382
Fluorides, heats of formation of.... 26

Fluorides, thermophysics of 134
Flux, amount needed in the blast furnace 251
Flux, behavior in the blast furnace 243
Flux, comparison of values of 263
Flux, required in Bessemer converter 346
Freeland, W. H., on smelting pyrrhotite 489, 515
Fuels, behavior of, in the blast furnace 236
Fuels, calorific power of 46
Fuels, comparison of values of 261
Fuels, utilization of, in the blast furnace 268
Fume, metallic 656
Furnaces, efficiency of 104
Furnaces, electric, efficiency of 640
Furnaces, electrolytic, definition of 534
Furnaces, electrolytic, for reducing alumina 658
Fusion of latent heats of, discussion 71
Fusion of latent heats of, tables 118–144
Fusion of matte 500
Fusion of slag 500

GALENA, roasting of 581
Gallium, thermophysics of 88
Gas, artificial 145
Gas, engine operation 226
Gas, mixed, producers for 158
Gas, natural, combustion of 10, 47, 53, 219
Gas, natural, from Iola, Kansas 636
Gas producers 381
Gases, composition of, from smelting furnace 497
Gases, pressure corrections for 7
Gases, relative volumes of 2
Gases, temperature corrections for 5
Gases, thermophysics of 141
Gases, waste, heat in 287
Gayley process of drying blast 330
Genoa, Marchesi's process at 539
Gin, G., in electrometallurgy of zinc 637
Glass, thermophysics of 141
Gold, behavior in the blast furnace 240
Gold bullion, refining of 610
Gold compounds, heats of formation of 18–40
Gold compounds, thermophysics of 131–144
Gold, metallurgy of 605
Gold, thermophysics of 100
Gold, vapor tension of 616
Gordon, F. W., slag calculations by 261
Goutal's method for calorific power of coal 503
Great Falls, Montana, copper refining at 566
Grüner's ideal working of a blast furnace 274

HABER, on reducing alumina 658
Hall, C. M., on reducing alumina 658
Halske and Siemens' copper process 555
Heat balance sheet of Bessemer converter 353
Heat balance sheet of blast furnace 281
Heat balance sheet of electrical furnace 433
Heat consumed in reductions 292
Heat of formation of chemical compounds 18–40
Heat of formation of slag 500
Heat of formation of some nitrates 510

Heat of formation of some oxides 579
Heat of formation of some sulfides 578
Heat properties of matte 500
Heat properties of slag 500
Heat units 14
Heats of formation 18
Herreshoff furnace, calculations on 489, 515
Hess, H. D., on open-hearth furnaces 395
Hixon's notes on matte smelting 526
Hoepfner's copper chloride process 557, 558
Hofman's Metallurgy of Lead 593
Hollaway, J., on bessemerizing matte 525
Hollaway, J., on oxidation of sphalerite 621
Hot blast, sensible heat in 285
Howe, H. M., notes on a bessemer charge 336
Hydrates, heats of formation of 19
Hydrides, heats of formation of 24
Hydrocarbons, combustion of 45, 217
Hydrocarbons, heats of formation of 24, 217
Hydrogen compounds, heats of formation of 18–40
Hydrogen compounds, thermophysics of 131–144
Hydrogen, thermophysics of 75
Hyposulfites, thermophysics of 136

Ice, specific heat of 119
Ideal working of a blast furnace, Grüner's 274
Ingalls, on cost of treating zinc ores 621
Ingalls, on oxidation of sphalerite 621
Insoluble anodes, use of 551
Iodides, thermophysics of 133
Iodine, thermophysics of 95
Iola, Kansas, natural gas from 636
Iridium, thermophysics of 99
Iron alloys, thermophysics of 113
Iron compounds, heats of formation of 18–40
Iron compounds, thermophysics of 125, 128–130
Iron, electric refining of 446
Iron, heat of oxidation of 352, 366
Iron ores, electrical reduction of 429
Iron oxide, discussion of reduction of 69
Iron oxide, problems concerning reduction of 128, 129
Iron oxides, heat absorbed in reducing 292
Iron persulfate process for copper ores 555
Iron sulfate solutions, resistivity of 559
Iron sulfide, heat absorbed in reducing 293
Iron, thermophysics of 85
Iron, use as soluble anode 548
Isabella, Tenn., pyritic smelting at 489
Isabella, Tenn., smelting of matte at 515

Jannettaz, "Les Cenvertisseurs pour le Cuivre" 526
Joplin, zinc ore from 620
Jüptner, data on furnace charges 403

Koch, on warm blast in smelting 487
Krafft, on the boiling of silver and gold 614

Laboratory of open-hearth furnaces 391
Laboratory of furnaces, efficiency of 414
La Lustre smelter, warm blast at 487

Landis, W. S., laboratory determinations by 500
Latent heats of fusion, discussion of 71
Latent heats of fusion, tables of 75–103, 118
Latent heats of vaporization, discussion of 73
Latent heats of vaporization, tables of 75–103, 118–144
Lead alloys, thermophysics of 109
Lead compounds, heats of formation of 18–40
Lead compounds, thermophysics of 131–144
Lead, electrometallurgy of 598
Lead, metallurgy of 578
Lead, physical constants of 583
Lead, refining of 583
Lead, thermophysics of 101
Lead, use as insoluble anode 551
Lead, vapor tension of 584
Lime, amount needed in Bessemer converter 347
Lime, heat in preheated 356
Lithium compounds, heats of formation of 18–40
Lithium compounds, thermophysics of 131–144
Lithium, thermophysics 76

MAGNESIUM compounds, heats of formation of 18–40
Magnesium compounds, thermophysics of 131–144
Magnesium, thermophysics of 80
Magnus, B., on energy losses at electrical contacts 562
Manganese, behavior in the blast furnace 240
Manganese compounds, heats of formation of 18–40
Manganese compounds, thermophysics of 131–144
Manganese, heat of oxidation of 371
Manganese, oxides, heat absorbed in reducing 293
Manganese, thermophysics of 85
Manhes, P., on bessemerizing matte 525
Marchesi, on electrolytic treatment of matte 539, 541
Marsh gas, mean specific heat of 142
Martin process 381
Matte, bessemerizing of 525
Matte, blister roasting of 523
Matte, bringing forward of 514
Matte, copper, composition of 469
Matte, electric furnace production of 574
Matte, electrolytic treatment of 539
Matte, grade obtained in smelting 474
Matte, thermophysical properties of 500
Maximum tension of aqueous vapor 121
Mayer, F., Das Bessemern von Kupfersteinen" 526
Mercury alloys, thermophysics of 113
Mercury compounds, heats of formation of 18–40
Mercury compounds, thermophysics 131–144
Mercury, metallurgy of 653
Mercury, thermophysics of 100
Mercury, vapor tension of 584
Metallic mist 656
Methane, mean specific heat of 142
Mine water, extraction of copper from 548
Mist, metallic 656
Moisture, heat absorbed in decomposing 293
Molybdenum compounds, heats of formation of 18–40
Molybdenum compounds, thermophysics of 131–144
Molybdenum, thermophysics of 91
Mond gas 169

Mond gas, superheating of 175
Monell process, problem concerning 424
Morgan producer, problem concerning 163
Mount Lyell, gases of furnace at 497
Mount Lyell, pyritic smelting at 488

NATURAL gas, combustion of 10, 47, 53, 219
Natural gas, from Iola, Kansas 636
Niagara Falls, Salem process as used at 599
Nickel alloys, thermophysics of 113
Nickel, behavior in the blast furnace 240
Nickel compounds, heats of formation of 18–40
Nickel compounds, thermophysics of 131–144
Nickel, heat of oxidation of 353, 374
Nickel, thermophysics of 86
Nickeliferous pyrrhotite, reduction of 435
Nitrates, heats of formation 30, 609
Nitrates, thermophysics of 137
Nitrides, heats of formation of 23
Nitrogen, thermophysics of 78

Oil, fuel, combustion of 219
Oil furnace, efficiency of 106
Open-hearth furnaces 381
Ore, behavior of, in the blast furnace 239
Ore, comparison of values of 265
Ore, electrical reduction of 429
Ores, copper, direct treatment by electrolysis 536
Osmium, thermophysics of 98
Oxides, heat absorbed in reducing 292
Oxides, heats of formation of 18, 579
Oxides, thermophysics of 118
Oxygen, thermophysics of 79

PALLADIUM compounds, heats of formation of 18–40
Palladium, thermophysics of 92
Paraffin, thermophysics of 142
Parrot Works, Butte, Bessemer process at 525
Peat, kiln drying of 227
Peters, "Modern Copper Smelting" 469, 526
Peters, "Principles of Copper Smelting" 469, 484, 566
Phosphates, heats of formation of 33
Phosphates, thermophysics of 138
Phosphides, heats of formation of 23
Phosphorus, behavior in the blast furnace 240
Phosphorus, heat of oxidation of 353, 377
Phosphorus, oxide, heat absorbed in reducing 293
Phosphorus, thermophysics of 81
Pig-iron, heat of formation of 285
Pig-iron, heat in melted 289
Platinum alloys, thermophysics of 113
Platinum compounds, heats of formation of 18–40
Platinum compounds, thermophysics of 131–144
Platinum, thermophysics of 99
Ports of an open-hearth furnace 388
Potassium compounds, heats of formation of 18–40
Potassium compounds, thermophysics of 131–144
Potassium, thermophysics of 83
Pot roasting, applicability to sphalerite 621
Pot roasting, principle of 586

Potter, H. N., on heat of formation of silica..... 353
Powdered coal, combustion of.....221, 223
Power obtainable from furnace gases..... 502
Power required to compress blast..... 313
Power, surplus, from blast furnace gases..... 272
Pressure of blast, methods of measuring..... 317
Pressure of blast, required in the Bessemer process..... 340

	Page		Page		Page
Problem 1.....	8	Problem 51.....	245	Problem 94.....	460
Problem 2.....	10	Problem 52.....	259	Problem 95.....	461
Problem 3.....	11	Problem 53.....	267	Problem 96.....	461
Problem 4.....	47	Problem 54.....	268	Problem 97.....	462
Problem 5.....	54	Problem 55.....	270	Problem 98.....	462
Problem 6.....	106	Problem 56.....	272	Problem 99.....	464
Problem 7.....	107	Problem 57.....	294	Problem 100.....	465
Problem 8.....	108	Problem 58.....	305	Problem 101.....	475
Problem 9.....	114	Problem 59.....	315	Problem 102.....	477
Problem 10.....	114	Problem 60.....	319	Problem 103.....	479
Problem 11.....	114	Problem 61.....	322	Problem 104.....	482
Problem 12.....	115	Problem 62.....	327	Problem 105.....	489
Problem 13.....	127	Problem 63.....	331	Problem 106.....	497
Problem 14.....	128	Problem 64.....	334	Problem 107.....	501
Problem 15.....	129	Problem 65.....	336	Problem 108.....	510
Problem 16.....	149	Problem 66.....	343	Problem 109.....	515
Problem 17.....	154	Problem 67.....	349	Problem 110.....	530
Problem 18.....	163	Problem 68.....	362	Problem 111.....	537
Problem 19.....	169	Problem 69.....	384	Problem 112.....	541
Problem 20.....	179	Problem 70.....	388	Problem 113.....	546
Problem 21.....	182	Problem 71.....	393	Problem 114.....	549
Problem 22.....	192	Problem 72.....	403	Problem 115.....	550
Problem 23.....	194	Problem 73.....	411	Problem 116.....	552
Problem 24.....	208	Problem 74.....	418	Problem 117.....	556
Problem 25.....	215	Problem 75.....	424	Problem 118.....	558
Problem 26.....	219	Problem 76.....	430	Problem 119.....	560
Problem 27.....	219	Problem 77.....	435	Problem 120.....	563
Problem 28.....	220	Problem 78.....	442	Problem 121.....	568
Problem 29.....	221	Problem 79.....	443	Problem 122.....	573
Problem 30.....	221	Problem 80.....	446	Problem 123.....	586
Problem 31.....	222	Problem 81.....	452	Problem 124.....	593
Problem 32.....	223	Problem 82.....	452	Problem 125.....	599
Problem 33.....	223	Problem 83.....	453	Problem 126.....	602
Problem 34.....	223	Problem 84.....	454	Problem 127.....	606
Problem 35.....	224	Problem 85.....	454	Problem 128.....	610
Problem 36.....	224	Problem 86.....	455	Problem 129.....	621
Problem 37.....	225	Problem 87.....	456	Problem 130.....	624
Problem 38.....	225	Problem 88.....	456	Problem 131.....	630
Problem 39.....	226	Problem 89.....	456	Problem 132.....	633
Problem 40.....	226	Problem 90.....	457	Problem 133.....	635
Problem 41.....	227	Problem 91.....	457	Problem 134.....	636
Problem 42.....	227	Problem 92.....	458	Problem 135.....	647
Problem 43.....	228	Problem 93.....	460	Problem 136.....	650
Problem 44.....	229			Problem 137.....	651
Problem 45.....	229			Problem 138.....	653
Problem 46.....	230			Problem 139.....	660
Problem 47.....	231				

PRODUCER gas, combustion of.....219, 227, 228, 229
Producers, gas.....246, 381
Pyritic smelting..... 483

Pyritic smelting, reaction at the focus 498
Pyritic smelting, slag produced by 487
Pyritic smelting, temperature attained in 485
Pyrrhotite, electrical reduction of 435
Pyrrhotite, smelting of 489

QUENEAU, on furnace efficiency 416, 423

RADIATION, heat 213
Radiation, from a Bessemer converter 533
Radiation, from a blast furnace 289
Radiation, from an electrolytic furnace 660
Radiation, from a roasting furnace 479, 482, 627
Radiation, from a smelting furnace 506
Radiation, heat, tables of 213
Radiation, heating by 392
Radium, thermophysics of 102
Reactions, double, in copper metallurgy 474
Reactions, double, in lead metallurgy 582
Recarburization, in the Bessemer converter 348
Reduction of iron ores electrically 429
Reduction of roasted lead ore 591
Reduction of zinc oxide 627
Refining, electrolytic, of copper 558
Refining, electrolytic, of gold 610
Refining, electrolytic, of iron 446
Refining, electrolytic, of lead 598
Refining, electrolytic, of silver 605
Refining, electrolytic, principles of 536
Refining, of impure lead 583
Regenerators, dimensions of 382
Regenerators, efficiency of 412
Resistivity of some solutions 559
Reverberatory smelting 501
Rhodium, thermophysics of 92
Richard, T. A., on pyrite smelting 484
Roasting, Bessemer, of lead ores 586
Roasting, heat generated in 477, 479
Roasting of lead sulfide 581, 586
Roasting of sphalerite 620
Roasting, removal of sulfur in 473
Roasting, smelting of copper matte 523
Rubber, thermophysics of 142
Rubidium, thermophysics of 90
Ruthenium, thermophysics of 91

SALOM, P. G., process for copper matte 545
Salom, P. G., process for reducing galena 598
Saulte Ste. Marie, electrical reduction at 435
Savelsberg pot-roasting operation 586
Schnabel "Handbook of Metallurgy" 469, 526
Schuller, on the boiling of silver and gold 615
Selenides, heats of formation of 22
Selenium, thermophysics of 89
Siemens and Halske's copper process 555
Siemens-Martin process 381
Siemens new-style furnace 418
Silica, behavior of, in the blast furnace 240
Silicates, heats of formation of 31

Silicates, thermophysics of 139
Silicides, heats of formation of 26
Silicon compounds, heats of formation of 18–40
Silicon compounds, thermophysics of 139
Silicon, heat of oxidation of 353, 369
Silicon, thermophysics of 81
Silver alloys, thermophysics of 113
Silver, analyses of impure 606
Silver, behavior in the blast furnace 240
Silver, compounds, heats of formation of 18–40
Silver compounds, thermophysics of 131–144
Silver, metallurgy of 605
Silver, thermophysics of 93
Silver, vapor tensions of 616
Slag, amount produced in the blast furnace 251
Slag, blast furnace, composition of 252
Slag, blast furnace, heat in 289
Slag formed in the Bessemer converter 346
Slag, fusion of, in the copper furnace 500
Slag, heat of formation of 286, 357
Slag, summation of ingredients of 254
Slag, thermophysics of 144
Smelting electric of copper ores 572
Smelting of lead ores 591
Smelting of zinc ores 637
Smelting, ordinary, of copper ores 499
Smelting, pyritic, rate of 489
Snyder, F. T., on efficiency of electric furnaces 640
Snyder, F. T., on electric zinc smelting 641
Sodium compounds, heats of formation of 18–40
Sodium compounds, thermophysics of 131–144
Sodium, thermophysics of 79
Solutions, extraction of copper from 548
Specific heats of chemical compounds 131–144
Specific heats of products of combustion 51
Specific heats of the elements 75–103
Speiss, formation of 592
Spence furnace, calculations on a 479
Sphalerite, roasting of 620
Steel, electrical production of 440
Steel furnace, efficiency of 114
Steel, thermophysics of 113
Sticht, analysis of furnace gases by 497
Sticht, on pyritic smelting 484
Stolberg, Marchesi's process at 539
Strontium compounds, heats of formation of 18–40
Strontium compounds, thermophysics of 131–144
Strontium, thermophysics of 90
Sulfates, heats of formation of 32
Sulfates, thermophysics of 136
Sulfides, heats of formation of 21, 578
Sulfides, thermophysics of 134
Sulfur, available in ordinary smelting 474
Sulfur, available in pyritic smelting 486
Sulfur, behavior in blast furnace 237
Sulfur, condition of, in roasted ore 475, 479, 507
Sulfur, heat absorbed in separation of 293
Sulfur, removal by partial roasting 473
Sulfur, thermophysics of 82
Sulfuric acid solutions, resistivity of 559

TANTALUM, thermophysics of 97
Tellurides, heats of formation of 22
Tellurium compounds, heats of formation of 18–40
Tellurium, thermophysics of 96
Temperature, theoretical, of combustion 50
Temperature, thermochemistry of high 61
Temperatures in the Bessemer converter 368
Temperatures in the blast furnace 308
Temperatures, using dry blast 312
Tension, maximum, of aqueous vapor 121
Thallium compounds, heats of formation of 18–40
Thallium compounds, thermophysics of 131–144
Thallium, thermophysics of 101
Thermochemical constants of bases and acids 38
Thermochemistry, applications of 13
Thermochemistry, calculations in 41
Thermochemistry of the Bessemer process 351
Thermophysics of alloys 109–113
Thermophysics of chemical compounds 118–144
Thermophysics of the elements 75–103
Thermit process, calculations 43
Thermit process, temperatures in 58
Thorium, thermophysics of 103
Tin alloys, thermophysics of 109
Tin compounds, heats of formation of 18–40
Tin compounds, thermophysics of 131–144
Tin, thermophysics of 94
Tissier, reduction of lead oxide by aluminium 585
Titanates, heats of formation of 34
Titanium, heat of oxidation of 353, 373
Titanium, thermophysics of 83
Toldt, data on furnace charge 403
Tungstates, heats of formation of 33
Tungsten compounds, thermophysics of 131–144
Tungsten, heat of oxidation of 353
Tungsten, thermophysics of 97

ULKE, modern electrolytic copper refining 469
Units, heat, definition of 14
Uranium, thermophysics of 103

VACUUM, volatility of gold and silver in a 614
Valves for open-hearth furnaces 388
Vanadium, heat of oxidation of 353
Vanadium, thermophysics of 84
Vancouver, B. C., electric zinc smelting at 641
Van Liew, on bessemerizing matte 530
Vapor, aqueous, maximum tension of 121
Vaporization, latent heats of, discussion 73
Vaporization, latent heats of, tables 75–103, 118–144
Vapor, metallic, calculation of weight of 618
Vapor, tension of cadmium 644
Vapor, tension of gold 615
Vapor, tension of lead 583
Vapor, tension of mercury 583
Vapor, tension of silver 615
Vapor, tension of zinc 643
Vattier, on electric smelting of copper ores 573
Volatility of lead 583
Volatility of silver and gold 614

Voltages of decomposition 547
Vulcanite, thermophysics of 142

WATER, cooling, heat in 290
Water gas 177
Water gas, combustion of 219
Water, heat of formation of 15
Water, thermophysics of 119
Water vapor, maximum tension of 121
Watts, O. P., on boiling points of silver and gold 615
Weightman, A. T., on treatment of copper matte 545
Welch process of copper concentration 514
Wohlwill process of refining gold bullion 610
Work done by blowing engines 313

ZINC alloys, thermophysics of 110
Zinc, behavior in the blast furnace 240
Zinc compounds, heats of formation of 18–40
Zinc compounds, thermophysics of 131–144
Zinc, distillation of 632
Zinc, distilling furnace, efficiency of 108
Zinc, electric reduction of 637
Zinc, heat of oxidation of 353
Zinc, metallurgy of 620
Zinc oxide, blast-furnace reduction of 651
Zinc oxide, electric reduction of 626
Zinc oxide, reduction of 63, 627
Zinc oxide, specific heat of 621
Zinc, reduction in a blast furnace 651
Zinc sulfide, roasting of 620
Zinc sulfide, specific heat of 621
Zinc sulfide, temperature of roasting 621
Zinc, thermophysics of 87
Zinc, vapor of 643
Zirconium, thermophysics of 90

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